SYNTHESIS OF WELL-DEFINED CYCLIC, BRANCHED, AND WATER-SOLUBLE POLYMERS VIA THE ANIONIC POLYMERIZATION OF 2-VINYLPYRIDINE

By
WILLIAM TOREKI III

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1988

TABLE OF CONTENTS

page

LIST OF ABBREVIATIONS iii

ABSTRACT iv

CHAPTERS

1 INTRODUCTION and BACKGROUND 1

General Considerations 1
Anionic Vinyl Polymerization 5
Macrocyclic Polymers 10
Star Polymers 16

2 EXPERIMENTAL 21

High Vacuum Anionic Polymerization Techniques 21
Purification of Solvents and Reagents 27
Synthesis of Living P2VP 36
Cyclization Reaction 41
Fractionation of Cyclic P2VP 46
Quaternization of P2VP 47
Three-arm Star P2VP by Coupling 48
Instrumental Methods 49

3 MACROCYCLIC POLY(2-VINYLPYRIDINE) 55

Cyclization Reaction- General Considerations 55
SEC Results 70
Viscosity Results 76
Glass Transition Temperatures 86

4 QUATERNIZATION OF CYCLIC AND LINEAR P2VP 98

General Considerations 98
Quaternization Reaction 100
Viscosities of Quaternized P2VP 106

5 THREE-ARM STAR P2VP BY COUPLING 115

6 PREPARATION OF TRIFUNCTIONAL CARBANION INITIATORS 128

7 SIDE REACTIONS IN LIVING P2VP SOLUTIONS 142

REFERENCES 160

BIOGRAPHICAL SKETCH 164

LIST OF ABBREVIATIONS

BuLi	butyllithium
DBX	1,4-bis(chloromethyl)benzene (dibromo-xylene)
DD^{-2}	1,1-dilithio-1,1,4,4-tetraphenyl-butane
DSC	Differential Scanning Calorimetry
2EP	2-ethylpyridine
2EPLi	2-ethylpyridyllithium
<G>	ratio of SEC peak molecular weights for two polymers having the same number of repeat units, but different geometries
<g'>	ratio of intrinsic viscosities (see <G>)
M, MW	molecular weight
M_w	weight average molecular weight
M_n	number average molecular weight
M_p	peak molecular weight from SEC
MWD	molecular weight distribution (M_w/M_n)
PDMS	poly(dimethylsiloxane)
P2VP	poly(2-vinylpyridine)
$<r^2>$	mean-square end-to-end distance of a polymer chain in solution
$<s^2>$	mean-square radius of gyration of a polymer chain in solution
SEC	Size Exclusion Chromatography
TCMB	1,3,5-tris(chloromethyl)benzene
T_g	glass transition temperature
THF	tetrahydrofuran
2VP	2-vinylpyridine
4VP	4-vinylpyridine

Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

SYNTHESIS OF WELL-DEFINED CYCLIC, BRANCHED, AND WATER-SOLUBLE POLYMERS VIA THE ANIONIC POLYMERIZATION OF 2-VINYLPYRIDINE

By

WILLIAM TOREKI III

APRIL 1988

Chairman: T. E. Hogen-Esch
Major Department: Chemistry

The techniques of anionic polymerization were used to synthesize star-branched and macrocyclic polymers of 2-vinylpyridine (2VP). These polymers were found to have narrow molecular weight distributions and a high degree of structural integrity. The polymers were characterized by size exclusion chromatography, dilute-solution viscometry, and thermal analysis. It was found that the hydrodynamic volumes of both types of polymers were less than the hydrodynamic volumes of linear polymers composed of the same number of monomer units. The glass transition temperatures of low molecular weight cyclic polymers of 2VP were found to be substantially higher than those of their linear analogs.

Cyclic and linear polymers of 2VP were converted into water-soluble polymers via reaction with methyl bromide. These quaternized polymers were analyzed by dilute solution

viscometry. The synthesis of water-soiubie poiyelectrolytes bas not been reported previousiy.

Attempts were made to prepare trifunctionel carbanion initiators for the polymerization of 2VP to give three-arm ster polymers. A well-defined trifunctionel carbanion was prepared end chereeterized, but it was found to be a poor initietor for 2VP due to steric interections which hinder the addition of monomer

During the couree of this work, the observetion wes made thet side-reactions which result in the couplieg of two polymer cheins occur in eolutione of living P2VP if they are stored at room tempereture. The neture of these side-reactions wes studied in detail.

CHAPTER 1

INTRODUCTION and BACKGROUND

General Considerations

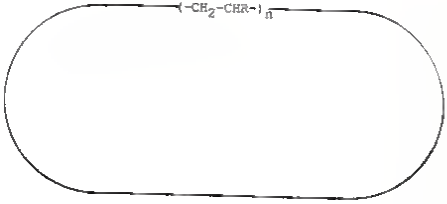
A better understanding of polymer structure/property relationships is perhaps the most important goal of a polymer chemist. The careful evaluation of these relationships depends on both the quality of the measurements of the physical properties of the polymer and the accuracy with which the polymer structure can be determined. Often, as in the case of naturally occuring polymers, the structures involved are very complex; and, although it may be possible to make a careful evaluation of the properties of a given polymer, the relationship of these properties to the polymer structure may be obscure due to either the complexity of the structure, or to a lack of understanding of the basic fundamentals of the system. In such cases, it is helpful, and often necessary, to first study simpler, well-defined systems in order to establish a clear and solid foundation upon which further, more detailed studies can be based.

One area of study in which this methodology is applicable is in the study of the effects that certain macromolecular architectural features have on polymer properties. The term "macromolecular architecture" refers to the manner in which individual polymer chains of a particular

chemical structure are linked together. One of the simplest types of macromolecular architecture is a linear chain. By adding other features such as branches or loops into the chain, the macromolecular architecture is made more complex and the physical properties of the polymer are changed. In order to gain a proper understanding of the effects of introducing such features into the macromolecule, these changes must be made in a uniform and controlled manner. That is, the changes should be made in such a manner that each individual molecule in a particular sample has an identical structure. This ensures that any measured properties will accurately reflect the changes under study. Since polymer samples are polydisperse (not all the chains in the sample are of equal length) it is often desirable to study narrow molecular weight distribution samples. By using monodisperse samples, differences due to the variation of molecular weight within a particular sample can be eliminated.

It is the goal of this work to study the synthesis and properties of polymers having two specific types of macromolecular architecture. The two types of polymers which are under investigation are macrocyclic polymers and three-arm star polymers. "Macrocyclic polymers" are polymers in which the molecules are in the form of large continuous loops, with no chain ends (see Figure 1a). "Three-arm star polymers" are polymers which are composed of three chains of equal length, joined together at one end by a central

a)



b)

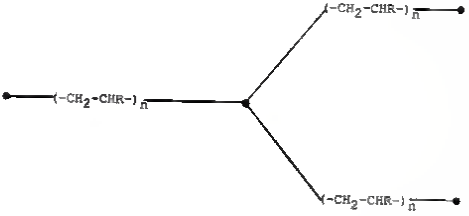


Figure 1 a) Macrocyclic vinyl polymer
b) Three-arm star vinyl polymer

branch point (see Figure 1b). The properties of such polymers will be compared to the properties of linear polymers having the same chemical structure and molecular weight. Polymers containing both of these types of structures have been prepared and studied before; however, more solid data is needed in order to fully develop the correlations between these kinds of structures and the physical properties of the polymers. By studying very well-defined polymers containing such structures, it may be possible to derive general fundamental structure/property relationships which will eventually lead to a better understanding of these types of systems, and of polymers in general. The study of ring-shaped molecules has been of interest for many years. By the early 1950's, properties of cyclic and linear polymers had been compared on a theoretical basis (1), but at this time there were no authentic samples of cyclic polymers available for study in order to confirm these theories. It has long been known that both cyclic and branched structures often occur in natural polymers such as proteins, DNA, and cyclodextrins (2,3), but, in more recent years several groups have attempted to synthesize macromolecules containing such structures. The syntheses of polymers containing well-defined branches and loops is by no means trivial, and by attempting to prepare such polymers, considerable advances in the area of synthetic polymer chemistry may be realized. In order to extract the maximum amount of useful information from these systems, it

is necessary that the structures studied be as well-defined as possible. That is, the macrocyclic samples should contain only cyclic chains, and not be contaminated by appreciable amounts (more than 5%) of linear material. The three-arm star polymers should be structurally homogeneous, with each molecule in the sample having exactly three arms of equal length. In both cases it is necessary that linear polymers with molecular weights identical to those of the star and cyclic polymers be available, in order to make valid comparisons of the properties associated with the various types of structures. The type of polymer used for the investigation should be one for which the polymerization chemistry is well understood and the polymer must be stable under a wide range of conditions, so that a wide range of physical properties may be studied.

Anionic Vinyl Polymerization

Anionic vinyl polymerization has proven to be a very useful technique for the preparation of polymers having controlled and well-defined structures. The usefulness of this method lies in the "living" nature of the polymers prepared anionically. This means that the active carbanionic centers, in contrast to most radical or cationic centers, persist throughout and even after the completion of the polymerization. As a result, all chains have an equal opportunity to grow, and this results in a monodisperse distribution of molecular weights. Moreover, the active chain ends may be utilized in a variety of different

reactions in order to produce many interesting end groups and architectures. Only vinyl monomers which can effectively stabilize a negative charge can be polymerized anionically. These include styrenes, acrylates and methacrylates, dienes, dimethylsiloxane, epoxides and 2- and 4-vinylpyridine, among others. Anionic vinyl polymerization begins with an initiation step (see Figure 2), in which a suitably reactive carbanion initiator reacts with the monomer, resulting in an adduct containing a carbanionic moiety which is electronically stabilized. The system (initiator, solvent, counterion, and temperature) must be designed so that this new active center is stable enough to remain in solution without undergoing side reactions or becoming deactivated. When new monomer is added to the solution, it can then react with this active site in a similar fashion, producing a new carbanionic active site identical to the first one. The propagation step (Figure 2) is generally not complicated by chain transfer reactions, and since all the growing chains propagate at the same rate, very narrow molecular weight distributions can be obtained. In general, anionic polymerization is not complicated by disproportionation or recombination reactions such as those present in radically polymerized systems (3). One characteristic of a true living polymerization is that there is a linear relationship between the amount of monomer consumed and the molecular weight of the polymer. There is however, one other important condition which must be satisfied

INITIATION:

PROPAGATION.

TERMINATION:

Figure 2. Anionic Vinyl Polymerization

in order to obtain narrow MWD polymers. Namely, it is imperative that the initiation step be faster than the ensuing propagation step. If the opposite is true, then a broad MWD polymer is obtained (4). Once all the available monomer has reacted, the living polymer chain stops growing and can usually be stored, under certain conditions, for long periods of time without deactivation. Subsequent addition of monomer to such a living polymer results in further chain growth. A second type of anionically polymerizable monomer can be added in order to produce block copolymers. Termination of the polymer results when the carbanion is deactivated by some type of reaction. Common termination reactions include protonation or alkylation. Due to the very reactive nature of the propagating species involved in anionic polymerization, extreme care must be taken to exclude water, oxygen or other deactivating species from the system during the polymerization. Through the use of multifunctional initiators and/or coupling agents, some very interesting types of macromolecular architecture may be obtained.

Styrene is one monomer, the anionic polymerization of which, has been extensively studied. The anionic polymerization of 2-vinylpyridine (2VP), a styrene analog (see Figure 3) has been studied in detail, but not as widely as that of styrene. Star and cyclic polymers of styrene have been prepared and studied (2,5), but no one has reported preparing such polymers from 2-vinylpyridine. It should be

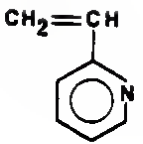


Figure 3. Structure of 2-vinylpyridine monomer

possible to prepare star and cyclic poly(2-vinylpyridine) (P2VP) via reactions similar to those which have been used for polystyrene. The use of 2VP rather than styrene has two distinct advanteges. First of all, since the 2-pyridyl carbanion is less basic than the styryl carbanion, and less reactive towards solvent, deactivating side reactions occur to a lesser degree. This is expected to result in a cleaner, better defined system, and allow the preparation of polymers having a higher degree of structural integrity. Secondly, P2VP can be quaternized by various reactions to give water-soluble polymers (6). The direct preparation of water-soluble polymers having a well-defined structure is, in most cases, not possible by other methods. Another potentially useful aspect of the living P2VP system is that, like the living polystyryl anion, the pyridine substituted carbanion intermediates show a very intense red color. This red color serves as a useful indicator in reactions requiring an exact stoichiometry.

Macrocyclic Polymers

Several different approaches have been used to prepare macrocyclic polymers. One method which has received much attention involves ring-chain equilibria, or "back-biting" reactions. This approach is the basis of the extensive work of Semlyan (2,7) on the synthesis and characterization of macrocyclic poly(dimethylsiloxane) (PDMS). This method involves the equilibrium polymerization of octamethylcyclotetrasiloxane with KOH. This leads to polydisperse samples

which may be fractionated to yield monodisperse samples of cyclic PDMS. The yield of cycles by this method decreases with increasing molecular weight. Cyclic poly(isobutylene) has been prepared by an insertion type of reaction wherein monomer units are sequentially incorporated into an ever expanding ring (8). This method produces polydisperse samples and again extensive fractionation is required in order to obtain narrow MWD cyclic polymers. Cycloalkanes having up to 100 carbon atoms have been prepared by metathesis reactions of cyclododecene followed by hydrogenation (9). None of these three methods produces well-defined, narrow MWD, high molecular weight cyclic polymers in high yield, nor do they provide exact linear molecular weight references for comparison to the cyclic polymers.

At least four separate groups have used the method of induced ring closure to prepare macrocyclic polystyrene (10-13). In this method, a difunctional anionic polymerization initiator is used to produce a narrow MWD chain having two living ends. This is then made to react with a difunctional coupling agent, resulting in cyclization. The possible reactions of a difunctional living polymer, $(P_1)^{-2}$, with a difunctional coupling agent, EX_2, are shown in Figure 4. It can be seen that both intramolecular reactions (leading to the formation of cyclic polymer), and intermolecular (or chain-extension) reactions may occur in such a system. The chain-extension reactions lead to the formation of a high molecular weight "polycondensate".

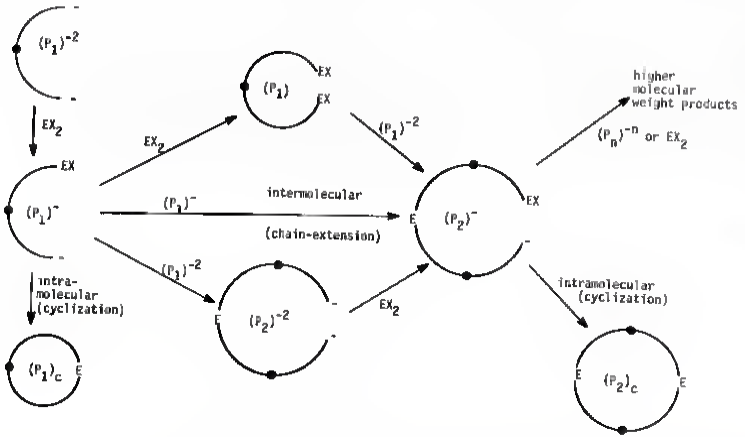


Figure 4. Possible reactions involving a difunctional living polymer, $(P_1)^{-2}$, and a difunctional electrophile, EX_2

Using this end-to-end cyclization method, cyclic polystyrenes with molecular weights up to several hundred thousand have been prepared (10). The cyclization yields (amount of cyclic polymer versus polycondensate) in these reactions were reported to range from 10 to 80%. This method has the advantage that in the absence of accidental termination reactions, only cyclic material with integral multiples of the precursor's molecular weight should be produced if an exact stoichiometric amount of coupling agent is used. This is in contrast to a broad continuous distribution of chain lengths, as is obtained in the other methods. Any chains which have become accidentally terminated on one end (by protic impurities for example) must necessarily be incorporated into the polycondensate. This point is discussed further Chapter 3. The relative amount of inter- vs. intramolecular reaction depends on the collision frequency of the different reactive chain ends. This collision frequency depends on the average distance between chain ends. The occurence of cyclization versus chain-extension reactions depends on whether the two chain ends which react with a given molecule of coupling agent are contained in the same or in different molecules. If the average separation between the chain ends of a difunctional living polymer is much less than the average distance between the polymer molecules in solution, then the cyclization reaction should be favored. As the concentration of living polymer molecules in the solution increases, the average distance

between the polymer molecules becomes less; therefore, the probability of intermolecular reactions increases. Thus, the easiest and most effective way to ensure that cyclization predominates over chain-extension, is to keep the concentrations of both the coupling agent and the living polymer very low. Attempts have been made to increase the cyclization yield in the preparation of macrocyclic polystyrene by addition of a nonsolvent in order to collapse the polymer coils, thus favoring cyclization, however, the observed increase in yield was very small (13).

Based upon the work of Jacobsen and Stockmayer, which contains a statistical analysis of the probability for intramolecular cyclization of a random-coil chain posessing two reactive ends (1), it is possible to derive a theoretical molar concentration of living chain ends (C_{eq}) at which the probability of inter- and intramolecular reactions are equal. This concentration is given by Equation I:

$$C_{eq} = 1000 * (3/2\pi)^{3/2} * 1/N_a * \langle r^2 \rangle^{-3/2} \qquad (I)$$

where

C_{eq} = concentration of living ends, (moles/L)

N_a = Avogadro's number

$\langle r^2 \rangle$ = mean square end-to-end distance of the polymer chain, (cm)

Theoretically, above C_{eq}, chain-extension is favored and below C_{eq} cyclization is favored. Note that molecular weight (M) does not appear in this equation; however, since the mean square end-to-end distance of a polymer chain,

$\langle r^2 \rangle$, is proportional to M under theta conditions (14,15), C_{eq} decreases according to $M^{-3/2}$. For P2VP chains in a theta solvent, this concentration is approximately 10^{-3} M for a chain of molecular weight 10,000, but decreases to 10^{-6} M for a chain of molecular weight 1,000,000. In order to obtain a good yield of cyclic polymer, the cyclization reaction should be carried out at a concentration below C_{eq}. Keep in mind that this concentration is only an approximation based on an ideal system, and may not account for the actual experimental situation. It can be used however, as a guide, in order to get a general idea of the concentration necessary in order to obtain a reasonable yield of cyclic polymer. Equation I predicts that a lower concentration of living ends (lower number of polymer molecules in the solution) is required in order to maintain the same ratio of intermolecular to intramolecular reactions as the molecular weight of the polymer is increased. This is easy to understand if one considers that as molecular weight increases, the average distance between the two ends of a given chain also increases. Thus, if the number of polymer molecules in the solution is held constant, it is obvious that the relative amount of intramolecular reaction (and hence the cyclization yield) should go down as molecular weight increases.

The primary goal of this work was to prepare cyclic P2VP by the end-to-end cyclization reaction of difunctional living P2VP. Well-defined cyclic polymers of 2VP having a

wide range of molecular weights have been prepared, characterized and compared to linear P2VP. Some of this work has already been reported in reference (16). The polymers have been characterized by size exclusion chromatography (SEC), dilute solution viscometry, and differential scanning calorimetry (DSC). The cyclic (and linear) polymers have been quaternized with various alkylhalides, and the properties of the resulting polyelectrolytes examined (17). The synthesis of well-defined, high molecular weight, water-soluble cyclic polyelectrolytes has never before been reported.

Star Polymers

The second goal of this work is to study the preparation and properties of well-defined three-arm star polymers of 2VP. There are two possible methods for the preparation of such polymers. The first method involves using a trifunctional carbanion to initiate the polymerization of 2VP. The resulting polymer would have three arms, each one possessing a living end. The second method involves the coupling of three monofunctional living polymer chains using a trifunctional coupling agent.

The preparation of three-arm star P2VP using a trifunctional initiator will be considered first. An ideal trifunctional carbanion initiator will result in the formation of a star polymer having three living arms of equal length, each with a living end. In order to obtain such a polymer, it is necessary to use an initiator which meets

three basic requirements. First of all, the initiator must be perfectly trifunctional. If any monofunctional or difunctional species capable of initiating polymerization are present in the system, then one- or two-armed polymer will also be produced. The second requirement is that, in order to obtain a narrow molecular weight distribution polymer, the propagation must proceed at a rate which is slower than, or comparable to, the slowest of the three initiation steps. In an ideal trifunctional initiator, all three initiation reactions should occur at the same rate. It is very possible, however, that reaction at the first or second site of a trifunctional carbanion will influence the reactivity of the remaining site(s). The effect of differences in reactivity of the three initiation sites will not be noticeable if the propagation rate is significantly slower than the slowest initiation step, because full initiation will occur before any significant amount of propagation. Three carbanionic sites contained in the same molecule can either be in direct resonance interaction with each other, or "insulated" from each other by one or more saturated carbons. If the sites are in direct resonance interaction with each other, the first initiation step will often be the fastest and the third step the slowest. If the three sites are insulated from each other, then they would be expected to have more nearly equal reactivities; however, electrostatic and inductive effects might still cause the first site to be the most reactive.

There are three general methods available for the preparation of trifunctional carbanions. The first involves the formation of a completely delocalized species such as the cycloheptatrienyl trianion (18) Studies of this initiator have not proven that it can be used to obtain star polymers. The second method involves addition of three moles of a strong nucleophile such as butyllithium to a molecule containing three suitably reactive vinyl groups. This method suffers from the drawback that "cross-linking" reactions may occur if the resulting adduct can react with remaining vinyl groups. This would result in a product which is not truly trifunctional. There have been reports of such systems being used for the polymerization of vinyl monomers (19), but there is little evidence that the polymers produced are well-defined three-arm stars. The third method involves the deprotonation of a molecule containing three relatively acidic hydrogens by a strong base such as butyllithium. In such a reaction it is imperative that the deprotonation be quantitative when a stoichiometric amount of the base is used, because excess base present in the system may also be capable of initiating polymerization. Gordon and Loftus (20) have prepared trilithiomesitylene by this method; however, it was not proven to be a satisfactory initiator for the preparation of living star polymers. In the present work, the goal was to synthesize a well-defined trifunctional carbanion initiator for the polymerization of 2-vinylpyridine that gives

well-defined three-arm living star polymers. This work is described, in part, in an earlier publication (21). The method used involved the synthesis of trifunctional analogs of initiators which are known to be useful initiators for 2VP (such as 2-ethylpyridyllithium and diphenylmethyllithium). This may be accomplished by linking together three such moieties through a central group (such as a 1,3,5-trisubstituted benzene).

There has been considerably more work done on the synthesis of star polymers via coupling reactions of living chains. There have been reports of the synthesis of star polymers containing from three to "thousands" of arms (5). The bulk of these reports offer no proof for the preparation of well-defined star polymers having a high degree of structural integrity. In this work, the synthesis of well-defined three-arm star polymers of P2VP by the coupling method was studied. Limiting the number of arms to only three simplifies matters and allows an easier and more reliable determination of the structural integrity and characteristics of such polymers. The basic approach is to prepare narrow molecular weight distribution polymers of 2VP using a monofunctional initiator and to then couple them using a trifunctional coupling agent. Two general types of coupling agents are possible. One is a compound which has three vinyl groups, to which the living ends can add (22). This type of coupling agent has the advantage that the resulting adduct is still a trifunctional

carbanion and further reactions can be carried out on the still living system. This type of coupling agent also has the disadvantage that crosslinking reactions may occur. The other type of coupling agent is one which possesses electrophilic groups (such as $PhCH_2Br$) which are capable of reacting with the living ends. Bryce et al. (23) have reported the preparation of three-arm star polymers of styrene, using 1,3,5-tris(chloromethyl)benzene (TCMB) as the coupling agent. The synthesis of well-defined star polymers of 2VP has not been reported previously. In this work, such polymers were prepared using TCMB as the coupling agent. This method for the preparation of star polymers has the advantage over the method of trifunctional initiation in that a portion of the linear precursor can be isolated and used as a reference for the molecular weight of the arms in the star polymer.

During the course of the work on the synthesis of star and cyclic P2VP, it was observed that side reactions occur in solutions of living P2VP in THF if they are not kept cold. These reactions appear to result in a coupling of chains to give a species having twice the molecular weight. These side reactions were investigated in some detail and will be discussed.

CHAPTER 2

EXPERIMENTAL

High Vacuum Anionic Polymerization Techniques

Due to the extremely reactive nature of the carbanion intermediates involved in anionic vinyl polymerizations, it is imperative that very rigorous conditions be used. These include the use of ultrapure reagents and solvents, scrupulously clean glassware, and the total exclusion of impurities such as oxygen and water vapor. High vacuum techniques are commonly used in order to maintain such conditions. The manipulations and procedures used to carry out a reaction under these conditions are in themselves somewhat of an art, and must be mastered before one can expect to obtain good results.

The heart of the system is the vacuum line itself (Figure 5). The vacuum system starts with a rotary oil pump capable of maintaining a forepressure of approximately 10^{-4} torr. The rotary pump is connected by a short length of heavy-walled rubber hose to the vacuum line, which consists of a "working", or manifold end, where the reaction vessels are attached, and a "system" end, which is comprised of a mercury or oil diffusion pump capable of maintaining an ultimate pressure on the order of 10^{-6} torr. Liquid nitrogen cold traps are used to remove volatiles

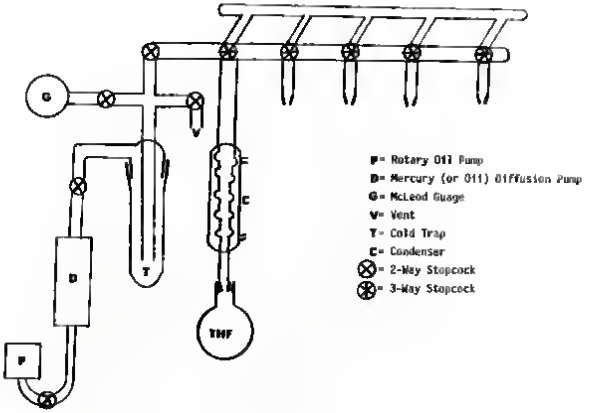


Figure 5. Schematic diagram of high-vacuum system

from the system, and a McLeod gauge is used to measure the pressure in the system. The line itself is constructed entirely of Pyrex, and the different components are fused together to form one continuous piece of glass. High precision Pyrex stopcocks are used throughout the system in order to close off various parts and permit the necessary manipulations.

The reaction vessels are constructed entirely of Pyrex and are fabricated or modified by use of a handheld natural gas/ oxygen torch. A reasonable amount of glass-blowing ability is necessary in order to construct, repair and maintain both the line itself and the various glassware used. Generally, one starts with a "blank" round-bottom flask (10-1000 ml.) to which various tubes, ampoules, frits, and ground glass joints are attached. In order to keep the various different reactants seperated from one another until they are ready to be mixed, the ampoules containing the reagents are equipped with a "breakseal". This consists of a small fragile glass pigtail (see Figure 6) which can be broken from outside the system by using a magnet to move a small glass-sealed iron rod placed inside, next to the breakseal. A quick swipe with the magnet is all that is required to break the seal and thus permit the contents to flow out. This method prevents the contamination which can often occur by using stopcocks for the addition of reagents. All glassware is scrupulously cleaned (using dilute (1%) HF if necessary), rinsed with

Figure 6. Diagram of glass breakseal used for addition of reagents under vacuum

water then acetone, and dried before being connected to the vacuum line. Once attached to the line and evacuated, the glassware is flamed with a torch for a few minutes to remove adsorbed water and oxygen from the glass surface. The entire vessel is then checked for leaks using a Tesla coil. Even the smallest pinholes are easily visible when the discharge from the coil passes through them.

Due to the very low pressure inside the system, it is very easy to transfer low boiling solvents and reagents by distilling them from one part of the system to another. This is accomplished by applying a cotton dauber cooled with either liquid nitrogen or an isopropanol/dry ice slurry to the part of the system where it is desired to condense the solvent. Sometimes, with high boiling reagents, it is necessary to facilitate this process by the appropriate application of slight heat supplied by a handheld warm air gun. This technique is very useful, for instance, to wash down the sides of a flask during a reaction.

Often, in this type of work, it is necessary to divide a large volume of a particular solution into 5-10 separate smaller ampoules. This is accomplished by using a divider as shown in Figure 7. Each ampoule is equipped with its own breakseal and a constriction. After the solution has been distributed among the various arms, the ampoules are cooled in a dry ice/isopropanol bath and the inside of the constrictions are rinsed with solvent (as described above). The ampoules are then sealed by a hand torch and removed.

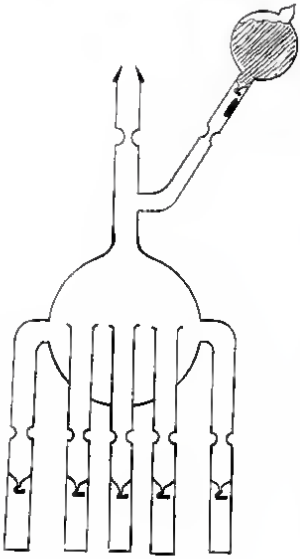


Figure 7. Apparatus used for division of a solution into several smaller ampoules

The washing down of the constrictions is important in order to remove any nonvolatile organic material which may pyrolyze when heated, causing pinholes in the glass as well as introducing impurities into the system. Even though extreme care is taken to prevent the introduction of impurities during the sealing process, a finite, but very small amount of deactivating species are always produced when a sealing operation is performed. For this reason, the sealing of glassware containing very small amounts of carbanion is best avoided.

Purification of Solvents and Reagents

Most of the reactions in this study were carried out in tetrahydrofuran (THF) solution. HPLC grade THF was refluxed over a sodium/potassium alloy for at least 24 hours and then distilled onto fresh alloy in a 3000 ml round bottom flask which was then flushed with argon and connected to the vacuum line. The THF was degassed several times and stored in this manner with continuous stirring for up to several months. The THF generally turned a deep blue color after contacting the finely dispersed alloy for several hours. This blue color is due to "solvated electrons" (4) and indicates the absence of any traces of water, oxygen or other impurities. Occasionally, when the blue color was hard to maintain due to a buildup of oxides or silicone grease in the THF, a small amount (0.5 g) of benzophenone was added. The deep purple color of the benzophenone dianion which rapidly formed confirmed the

absance of reactive impurities. Hexane waa purified and stored in a similar manner; however, no color changes are observed with hexane.

The methods used for the purification of many of the reactants used are quite similar. A general procedure is illustrated here for the purification of 2-vinylpyridine (2VP). Procedures for many of the other chemicals used including: 2-ethylpyridine, 2-methylpyridine, 1,1-diphenylethylene, alpha-methylstyrene, mesitylene, and diphenylmethane are quite similar. Reagent grade 2VP was fractionally distilled under vacuum (80°C/30 torr) and the middle 60% was collected. This was then stirred over CaH_2(s) overnight and the flask was connected to an apparatus such as that shown in Figure 8. The 2VP was frozen by immersing the flask in liquid nitrogen, then allowed to degas and thaw under vacuum. Repeated cycles of freezing and thawing combined with thorough degassing were used. The 2VP was then allowed to distill into a glass bulb equipped with a breakseal which was then sealed off and removed. The contents of the bulb was divided among several smaller bulbs as described above. For most work, such a purification was sufficient; however, in some cases (particularly for the case of monomer to be used in the preparation of a very high molecular weight polymer) further purification was deemed necessary. This was accomplished by attaching the sealed bulb of material to an apparatus like that shown Figure 9. A small piece of

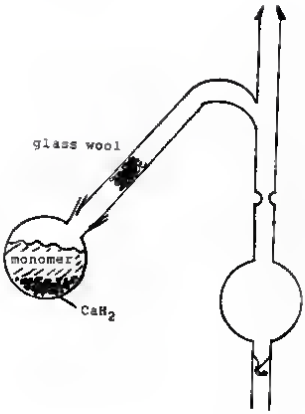


Figure 8. Apparatus used for preliminary drying of 2VP monomer, using CaH_2

potassium metal was placed in flask A, which was then sealed and evacuated. By heating the flask gently with a torch, a finely divided mirrorlike coating of metal on the bottom of the flask could be produced. The 2VP was then introduced onto this metal surface. The monomer was allowed to react for approximately 20 minutes with gentle stirring before it was distilled into a side arm and sealed off. The resulting monomer was extremely pure, as demonstrated by the excellent results obtained (see Chapter 3).

Methyl iodide was stirred over CaH_2(s) and stored in a round bottom flask equipped with a stopcock and a ground glass joint. This setup was useful for the routine use of this reagent, as it could be stored in the freezer and attached quickly to the vacuum line and used as needed.

Alkali metals (sodium, lithium, and potassium) were cleaned by dipping freshly cut chunks of the metal successively in hexane, isopropanol (or methanol for lithium) and then THF. This process gave pieces of metal with clean and reactive surfaces.

Butyllithium was used as 1.6 M solutions in hydrocarbon solvent (Aldrich). The exact concentration of BuLi in these solutions was determined by reacting them with a known amount of excess triphenylmethane or fluorene in THF at $-78^{\circ}C$, followed by quenching with methyl iodide. The ratio of methylated to parent hydrocarbon was then determined by capillary GC. From this data, the exact

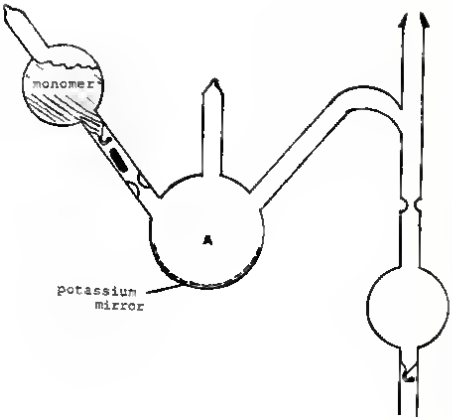


Figure 9. Apparatus used for purification of 2VP monomer over potassium mirror

concentration of the butyllithium solution could be calculated.

Impure 1,4-bis(bromomethyl)benzene (DBX) (Aldrich) was purified by recrystallization in either methanol, THF or petroleum ether. The recrystallization was repeated until GC analysis showed that the purity was greater than 99%. This usually took from 4-7 times. The product was then dried for 24 hours on the vacuum line (mp = 142°C).

The synthesis of 1-lithio-1-(2-pyridyl)ethane (2EPLi) was accomplished by reacting 2EP (~4 ml) with a 1.1 molar excess of nBuLi in THF (~50 ml) at -78°C until the red color of the 2EPLi appeared to be fully developed (~30 minutes). The flask was then slowly warmed to room temperature and the solution was degassed to remove butane. The solution was then transfered to a breakseal equipped bulb and sealed. This solution was purified by recrystallization in the apparatus shown in Figure 10. The crude 2EPLi solution was introduced into the main flask (A), and the THF was removed by distillation until only a small amount (~10 ml) of solvent remained. Approximately 40 ml of dried hexane was then added to the 2EPLi residue. The apparatus was then placed in a freezer at -20°C until crystallization occurred. Solvent was then decanted into the side flask and the crystals were washed with solvent which was back-distilled into the main flask. After two or three washings, the side bulb was sealed off and the crystals were dissolved in fresh THF. The purified 2EPLi solution

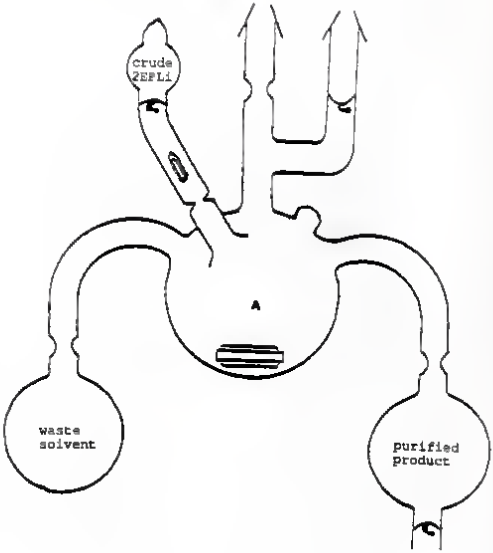


Figure 10. Apparatus used for recrystallization of 2EPLi

was then sealed into a breakseal equipped bulb and later divided as necessary for use.

The difunctional initiator, 1,4-dilithio-1,1,4,4-tetraphenylbutane (DD^{-2}) was prepared by reacting 1,1-diphenylethylene with excess lithium metal in THF for 24 hours at room temperature (4,21). The deep red solution was filtered through a sintered glass frit into a breakseal bulb and sealed. The solution was then recrystallized in the same manner as for 2EFLi, except that the recrystallization solvent was a mixture of approximately 40% THF and 60% hexane. The purity of the DD^{-2} solution was checked by reacting a portion of it with excess CH_3I. This results in methylation of the carbanionic centers. The product of this reaction was analyzed by capillary GC. If there was any monofunctional carbanion present in the initiator solution, then the monomethylated product was clearly visible in the chromatogram. Generally, if the synthesis and recrystallization were done correctly, there was less than one percent monofunctional anion present.

Solutions of oligomeric dianions of alpha-methylstyrene were prepared in a manner analogous to the preparation of DD^{-2}, except that alpha-methylstyrene was used rather than diphenylethylene, and potassium metal was used rather than lithium (4,21). Gas chromatographic analysis of the reaction mixture showed that it contained predominantly dimer, with small amounts of trimer and tetramer also present.

The synthesis of 1,3,5-tris(chloromethyl)benzene (TCMB) was accomplished according to the procedure of Bryce et al. (23), which involved reacting mesitylene with 1,3-dichloro-5,5-dimethylhydantoin in CCl_4. The product was purified by recrystallization from petroleum ether. Structure and purity were confirmed by NMR and GC, respectively. The final purity was found to be greater than 99% (m.p.= 57°C).

^1H NMR: 4.4 ppm, singlet, (2H); 7.2 ppm, singlet, (1H).

The synthesis of 1,3,5-tris[2-(2'-pyridyl)ethyl]-benzene (TEPB) was accomplished by reacting an excess of 2-methylpyridyllithium (prepared from 2-methylpyridine and n-butyllithium) with TCMB (21). This compound was purified by preparative HPLC and recrystallized in hexane. Structure and purity (greater than 99%) were confirmed by NMR and GC respectively.

^1H NMR: 3.0 ppm, singlet, (4H); 7.3 ppm, multiplet, (4H);
8.6 ppm, doublet, (1H).

The compound, 1,3,5-tris[(2,2-diphenyl)ethyl]benzene (TDEB) was prepared by reacting TCMB with an excess of diphenylmethyllithium (prepared from diphenylmethane and n-butyllithium) (21). This was recrystallized by dissolving the compound in cyclohexane followed by addition of an equal volume of n-hexane. Structure and purity (>99%) were confirmed by NMR and GC respectively. (m.p.= 97-99°C)

^1H NMR: 3.2 ppm, doublet, (3H); 3.9 ppm, triplet, (1H)
6.4 ppm, singlet, (1H); 7.2 ppm, multiplet, (10H).

The synthesis of 1,3,5-tris[(3,3-diphenyl)propyl]-benzene (TDP3) was accomplished by reacting excess 1,1-diphanylethylene with a solution containing trilithiated mesitylene which had been prepared by the method of Klein et al. (24). The reaction mixture was then quenched with methanol. The product was purified by preparative HPLC. Purity was found to be greater than 95% by GC analysis. The structure was confirmed by NMR. The final product was a glassy solid which could not be recrystallyzed.

^{1}H NMR: 2.5 ppm, multiplet, (4H); 3.8 ppm, triplet, (1H); 6.7 ppm, singlet, (1H); 7.2 ppm, multiplet, (10H).

Concentrations of all carbanion solutions were determined (when necessary) either by UV spectrophotometry (if the molar absorptivity was known) or by reaction with excess triphenylmethane or fluorene followed by quenching with methyl iodide and GC analysis, as described under purification of butyllithium.

Synthesis of Living P2VP

The following is a typical procedure used to make solutions of living P2VP in THF. The procedure is a general one, and can be modified as necessary depending on the requirements of a particular experiment. The described procedure produces a solution (~60 ml) containing about 5 grams of polymer with a molecular weight of approximately 10,000 (DP=100), but different molecular weights, or concentrations of polymer, can be obtained by varying the amount of monomer and initiator used. Several additional

steps were taken (see below) when it was desired to produce polymers with very high molecular weights (greater than 100,000). Note that this procedure is applicable for the preparation of both one-ended and two-ended living P2VP. A reaction apparatus such as the one shown in Figure 11 was used. The flask was evacuated, checked for leaks, and flamed. The breakseal containing the initiator solution ($5x10^{-4}$ moles) was broken and the contents were allowed to flow into the bottom of the flask. The flask was then cooled in dry ice and THF was distilled in until the total volume of initiator solution was approximately 60 ml. As the THF was being added, a cold dauber was used to assist in washing traces of initiator left in the upper portions of the apparatus down into the solution. Once all the solvent was added, the solution was cooled to -78°C, and mild heating was applied to the monomer inlet tube at point A with a hot air gun. The level of the cooling solution (dry ice/isopropanol) was kept below the solvent level inside the flask in order to prevent monomer vapor from condensing on the walls of the flask. The breakseal containing the 2VP monomer (~5 ml) was broken and the contents were allowed to distill slowly into the rapidly stirring solution. The heating applied to point A helps to ensure that the monomer vapor distills directly into the solution without condensing on the walls of the flask. Since the bulb containing the monomer tends to cool as distillation occurs, it was immersed in a room temperature water bath to

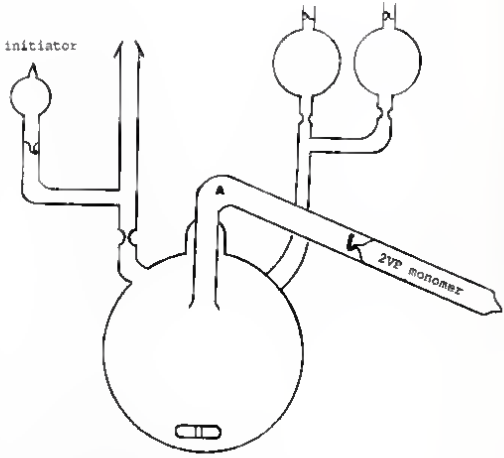


Figure 11. Apparatus used for the preparation of living P2VP solutions

ensure a constent rate of eddition. Great care wes taken to make sure that there were no traces of initietor on the tip of the monomer iniet tube, es clogging, due to premature polymerization, would occur. Additional dry ice was added to the cooling bath during the polymerizetion in order to ensure thet the temperature was mainteined at -78°C. Megnetic stirring wes maintained in order to ensure uniform dispersion of monomer vapor into the soiution. A gless stir ber wes used, rather than a teflon one, because the initiator reects with teflon, and thus becomes partieiiy deactiveted. The system wee opened to the vecuum line e couple of times during the polymerization in order to maintein en optimum vecuum. Upon completion of the eddition of monomer, the solution waa eiiowed to stir for a few minutes end then degessed a finai time. At this point the reaction wes complete and the iiving polymer aolution was either termineted or seaied in e breakseai bulb so that it couid be used in another reection. It is very important that eny menipuietions performed on the iiving polymer solutions are done so as to not let the temperature of the solutions riee much above -78°C, aa side reections may occur, however, when kept at -78°C the soiutions ere stabie for et leeet a few deye, and probebly much longer.

Sometimee, when it wes necessary to prepare e polymer of very high moieculer weight, or if for some other reason a very small amount of initiator wes being used, the procedure waa modified as foilowe. The entire epparetus, after

being evacueted and sealed, was rinsed with a diiute carbanion eoiution to remove any reactive impurities from the glass, ae well as the solvent. This soiution was then poured into a side arm and any traces of carbanion remaining in the epparetus were then rinsed out with soivent distiiled back from the side arm. When aii of the carbanion had been rinsed into the side arm, the solvent was distiiied back into the reaction flask, and the side-arm containing the dry carbenion residue wee very carefuliy seaied off end removed. The poiymerization reaction was then carried out es before. This procedure ia a very effective way to obtain conditions resulting in very iittie termination due to solvent impurities.

Poiy(2-vinylpyridine), after terminetion, can be purified by dissoiving it in an organic solvent such as chioroform, and then extracting the polymer with diiute aqueous HCi. This separatee the polymer from neutrai organic impurities which remain in the organic layer. The polymer ie then recovered by neutraiizing the aqueous ieyer with KOH, and extracting the polymer with fresh chioroform, thus separating the poiymer from ionic contaminants. The organic layer is then dried and concentrated until it contains about i0-20% polymer. This solution is then fiitered and added dropwise to a large voiume of rapidiy stirred hexane. This produces e fine white precipitate of P2VP. Coiiection of the precipitate is facilitated by adding a few drops of methenoi to the suspension untii it

agglomerates. The resulting polymer is then collected and dried in a vacuum oven for 24 hours at a temperature not exceeding 80°C.

Cyclization Reaction

Difunctional living P2VP was prepared according to the procedure outlined above, using DD^{-2} as the initiator. The living solution was divided into two portions. One portion, (~10 ml) was sealed in a breakseal-equipped ampoule and later protonated with degassed methenol, which was distilled into the ampoule through the vacuum line. This gives a linear polymer which can be used as an exact SEC molecular weight reference for the cyclic polymer. The other portion (~50 ml) was placed in a breakseal bulb and used in the cyclization reaction. Great care was taken during the dividing and sealing procedures to always keep the solutions as cold as possible (less than -40°C). The bulb containing the living polymer solution was attached to the reaction apparatus as shown in Figure 12. The carbanion wash solution and the coupling agent solution had been previously prepared and attached to the apparatus (see below for the preparation of the coupling agent solution). A cone of aluminum foil was placed around the bulb containing the polymer solution once it was attached to the apparatus. This cone was then filled with crushed dry ice in order to keep the solution cold until it was needed for the reaction. The apparatus was attached to the vacuum line, evacuated, checked for leaks, and flamed. The

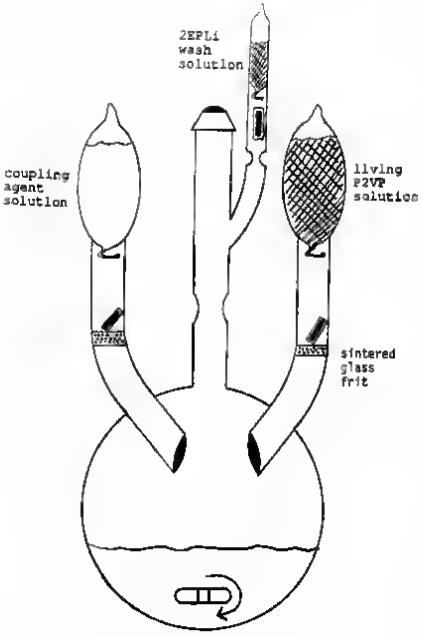


Figure 12. Apparatus used for the cyclization of difunctional living P2VP

carbanion wash solution (2EPLi) was added to the flask and then approximately 150 ml of THF was distilled in. The flask was cooled and sealed from the line. The entire inner surface of the apparatus was rinsed with the carbanion solution which was then rinsed down into the bottom of the flask. The apparatus was clamped in an upright position and magnetically stirred at the fastest possible rate. The aluminum foil and dry ice were removed from the living polymer bulb which was allowed to slowly warm. The breakseal containing the coupling agent solution was broken and it was allowed to slowly drip into the reaction flask. The coupling agent reacted with the excess carbanion from the wash solution to form a 2:1 adduct of 2EP and DBX. The presence of a small amount of this product in no way affected the cyclization reaction, and it could be easily removed from the product at the end of the reaction, when the polymer was precipitated. When the red color of the wash solution had just disappeared, the breakseal containing the living polymer was broken, and the two solutions were allowed to slowly drip into the rapidly stirred reaction flask. The rate of addition of either the living polymer or the coupling agent solution could be controlled by a light heating or cooling applied to the appropriate part of the reaction apparatus. The rates of addition were adjusted so as to maintain a slight excess of living polymer in the flask at all times, as evidenced by a faint red color from the P2VP living ends. The solutions were added

at a rate of approximately one or two drops per second. The total time required for the addition was less than thirty minutes. Due to differences in the viscosities of the two solutions being added, glass frits of different porosities were used in order to make it easier to add the reagents at identical rates. The concentration of living ends in the reaction flask was estimated to be on the order of 10^{-6}M on the basis of visual comparison to solutions, the exact concentrations of which had been determined by UV spectrophotometry. In most cases the amount of coupling agent available exceeded the amount needed for the reaction, in order that all of the living polymer solution could be used. Upon completion of the reaction, the flask was opened, the solution was removed, concentrated on a rotary evaporator, and precipitated as described above.

The DBX coupling solution described above had been prepared ahead of time in an apparatus like the one pictured in Figure 13. The appropriate amount of purified DBX crystals were weighed into a small breakseal ampoule which was then evacuated and sealed. This ampoule was then attached to the apparatus as shown. The apparatus was then placed on the vacuum line, THF was distilled into bulb A, the 2EFLi wash solution was added, and the apparatus was sealed. After washing the entire apparatus, the dilute carbanion solution was poured back into flask A, then the solvent was distilled into flask B which was cooled to -78^{o}C and carefully sealed. The breakseal containing the

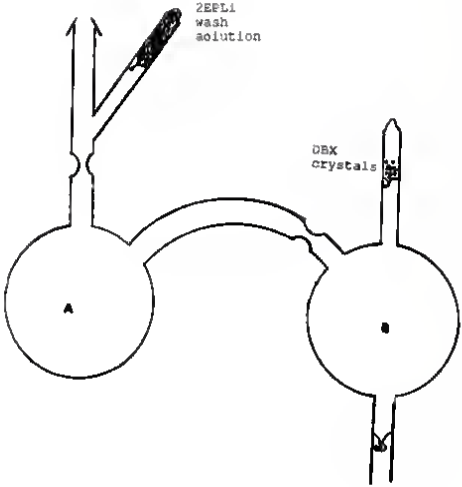


Figure 13. Apparatus used for the preparation of DBX coupling agent solution.

DBX crystals was broken and they were allowed to dissolve in the THF. The total volume of solution used in each cyclization reaction was between 50 and 100 ml.

Fractionation of Cyclic P2VP

The crude product from the cyclization reaction was subjected to fractional precipitation in order to separate the cyclic material from the polycondensate. The crude product mixture (approx. 5 grams) was dissolved in 15-20 ml of chloroform. The solution was stirred rapidly and hexane was added dropwise until a precipitate was observed. Continued addition of hexane resulted in the formation of two distinct phases. The lower phase, which was very viscous, tended to stick to the bottom of the flask and comprised less than 10% of the total volume of the solution. SEC analysis showed that the lower phase was enriched in polycondensate, while the upper phase was enriched in cyclic polymer. By adding more hexane, stirring vigorously to ensure complete equilibration between the phases, allowing the lower phase to settle out, and analyzing the upper phase by SEC, eventually an upper phase which contained only the low molecular weight fraction could be obtained. This was then decanted, and the lower phase was redissolved in a small amount of chloroform and refractionated to obtain a second portion of purified cyclic polymer. This process was repeated about three or four times with diminishing returns. The supernatants were combined and analyzed by SEC to test the overall sharpness of the

fractionation. The solution was then concentrated, precipitated in hexane, and dried in a vacuum oven. In this manner, up to a gram of purified cyclic polymer could be obtained from 4 to 5 grams of starting material with a 50% cyclic polymer content.

One crude sample was subjected to fractionation by SEC. Appropriate fractions of the eluent from the SEC column were collected from repeated injections of crude product. The purity of the cyclic material obtained in this manner was excellent; however, only very small amounts (less than 10 mg) could be obtained for each injection. Preparative scale SEC would be very useful in this regard.

Quaternization of P2VP

The following procedure was used to convert P2VP (cyclic or linear) into a water-soluble polymer. The polymer (0.10 to 0.50 g) was weighed into a heavy-walled glass tube equipped with a ground-glass joint for attachment to the vacuum line. The polymer was then dissolved in approximately 20 ml of solvent. The solvents used included nitromethane, N,N-dimethylformamide, sulfolane and THF. The THF was purified as described above and added to the reaction tubes by distillation through the vacuum line. The other solvents were reagent grade, and were used straight from the bottle, without further purification. The alkylhalides used (CH_3I, CH_3Br, or CH_3CH_2Br) were dried by stirring them over CaH_2(s), then added to the reaction tubes by distillation through the vacuum line. A tenfold

excess of alkylhalida, relative to polymer, was used in all cases. After mixing, the solutions were frozen by immersing the tubes in liquid nitrogen. Thay were then degaased and allowed to thaw. This freeze degassing was repeated twice, than the tubes were sealed and removed from the vacuum line. The sealed tubes were then placed in a water bath at a specified tampereture (25°C to 100°C) for specified lengths of tima (6 to 24 hours). In all casas, a white precipitate formed in the tube during the course of the reaction. After the specified reaction time had elapsad, the tubes were allowad to cool and the contents wera diesolved in methanol. The solvant and excess alkyl halide ware then removed under vacuum. The residue was dissolved in a few milliliters of methanol, filtered, and precipitated in diethyl ether. The pracipitate wea then collected and dried in a vacuum oven at 50°C. The products were completaly soluble in methenol and water, but insoluble in most organic solvents. Samples of tha producta were sent to Atlantic Microlabs (Atlanta Ga.) for % Br anelyais.

Three-arm Star P2VP by Coupling

Three-arm star P2VP was prepared by coupling living (one-anded) P2VP with TCMB. Solutions of living P2VP were prepared as described above. The coupling agent solution was prepared by dissolving the required amount of TCMB in THF (50 ml),in a mannar eimilar to that described above for DBX solutions. The apparatus used for tha reaction is

similar to that shown in Figure 11, except the flask was equipped with a sintered glass frit used for addition of the coupling agent. The living polymer was made directly in the apparatus pictured, using 2EPLi as the initiator. When the addition of monomer was complete, the coupling agent was added to the stirred solution by allowing it to drip through the glass frit. Approximately 80-90% of the required amount of coupling agent was added rapidly, and allowed to react before the addition was continued. The rate of addition of the coupling agent was controlled by application of slight heating or cooling to the appropriate part of the apparatus. The course of the reaction could be followed by monitoring the red color of the living P2VP solution. The remainder of the coupling agent was added dropwise, thus ensuring that a stoichiometric amount of TCMB was added. The TCMB was added very slowly at the end, until the red color just disappeared. The flask was then opened, and the polymer was collected as described above.

Instrumental Methods

Size exclusion chromatography (SEC) was done using a 60 cm x 7.5 mm Phenogel (either MXM or MXH) column which was custom packed by Phenomenex Co. (Palos Verdes CA). It is a cross-linked polystyrene gel column suitable for use with a wide variety of organic solvents. The eluting solvent was THF. One percent by volume of triethylamine was added to the THF in order to prevent adsorption of P2VP onto the column (25). Flow rates ranged from 0.7 to 2.0

ml/min. A Waters model 6000A HPLC pump and model U6K injector were used. Detection was by a Perkin Elmer LC-75 UV detector set at 268 nm. Polymer concentrations in the solutions analyzed ranged from 0.05 to 0.25% (w/v) and injection volumes were from 5 to 50 microliters. All solutions analyzed were filtered through a 0.5 micrometer filter prior to injection. The detector was interfaced to a Zenith PC-100 computer equipped with a Dascon-1 data collection system, which operated at the rate of 1 Hz. This allowed direct calculation of molecular weights and molecular weight distributions and permitted the normalization and superimposition of different runs. The BASIC computer programs for data aquisition, molecular weight calibration, computation of molecular weight averages, and graphic display of the results were written specifically for this work. The programs for the calculation of molecular weight averages were similar in nature and method to the computation method, named "GPCV2", which has been described by Yau (26). This method allows for corrections due to band broadening in the column. Molecular weight calibration was done using narrow molecular weight distribution P2VP and polystyrene standards (Polysciences Inc., Pressure Chemical Co., Waters Associates, or Scientific Polymer Products Inc.). The manufacturer's values of polydispersity were used to calculate the band-broadening correction factors for the system. There was some scatter in the correction factors calculated in this manner, so a number closer to

the lowest value of the correction factor, rather than the average value, was used. This helped to avoid overcorrection when calculating molecular weight distributions. Analysis of a truly monodisperse molecule (1,3,5-tris[(2,2-diphenyl)ethyl]benzene; MW = 618) using such correction factors gave a M_w/M_n value of 1.01 for this molecule. Such a result is consistent with this conservative methodology. Both P2VP and polystyrene standards were used for molecular weight calibration. Both types of standards were seen to fall on the same line when Log(MW) was plotted against elution volume, and such plots had correlation coefficents of 0.995 or greater. It was noted both here and in the literature (25), that with other column/ solvent combinations, the calibration plots for P2VP and polystyrene are distinctly different from each other. The current finding that the curves for the two polymers exactly coincide is most likely due to the novel solvent system which was used. The role that the added Et_3N plays in determining the elution volume of the polymers has not been fully elucidated, but it is clear that this solvent system gives excellent results.

The retention times for the polymer samples which were analyzed by SEC ranged from approximately 400 to 800 seconds. The times were recorded to the nearest second, and were found not to vary by more than one second for multiple determinations of a given sample. For a retention time of 500 seconds, this corresponds to a relative error

or +/- 0.2% in the measurement of the elution volume. The relative error in the slope calculated for the calibration curve is thus approximately +/- 0.4% (neglecting the unknown degree of accuracy in the molecular weights of the calibration standards). These combined errors lead to a maximum precision of approximately +/- 1.5% in the calculated values of molecular weight (depending on the flow rate, and the molecular weight of the sample). In this work, the ratio of two experimentally determined molecular weights was often of significant importance (see chapter 3). The minimum relative error in such a ratio comes out to be approximately +/- 2.2% (which corresponds to an absolute error of +/- 0.02 when the ratio of molecular weights is 0.75).

Capillary gas chromatographic analysis (GC) was performed on a Hewlett-Packard model 5880A gas chromatograph equipped with a microprocessor, flame ionization detector, and temperature programmable oven. The column used was a 50 meter SE-54 capillary column (0.2mm i.d.), and helium was used as the carrier gas. This system is extremely sensitive and is capable of providing excellent analyses on a wide variety of different types of low molecular weight samples.

Ultraviolet spectrophotometry was used for determination of the concentration of some carbanion solutions using Beer's Law and published values of molar absorptivity. Either a Beckman Acta-V or a Perkin Elmer Lambda-9 system

were used. Quartz cells having a 2 mm path length were used, in conjunction with 1.9 mm spacers. The solution path lengths were calibrated using known standard solutions of K_2CrO_4. Each cell was equipped with a quartz to pyrex graded seal for attachment to a vacuum apparatus. All measurements on carbanion solutions were done under vacuum.

Preparative scale HPLC was used in some cases to purify reaction products such as TCMB or TEPB. An Altex model 420 programmable gradient system, fitted with a constant wavelength UV detector was used. The column was a Merck Lobar-B packed with 40-63um LiChroprep Si60 silica gel. Generally the eluting solvents were programmed from nonpolar (hexane) to polar (4:1 CH_2Cl_2 : CH_3OH) over a period of 20-200 minutes depending on the sample. Such a system is useful for the preparation of multigram quantities of material.

Thermal analysis (DSC) was performed on a Perkin-Elmer DSC-7 thermal analyzer combined with a Perkin-Elmer 7500 series professional computer. The P2VP samples were placed in sealed aluminum sample pans for analysis. In order to assure identical thermal hysteresis for all the samples, they were heated to 200°C, then cooled at a rate of 20°C/min to 55°C. The samples were then heated from 55°C to 135°C at a rate of 20°C/min. In most cases, the glass transition occured around 100°C. The values of the glass transition temperature were calculated by the

computer and were found to be reproducible to within approximately 0.5°C.

Proton and carbon-13 NMR were used in some cases for structural confirmation and analysis of reaction products. These measurements were taken either on a Varian EM360L (60 MHz) or XL200 (200 MHz) NMR spectrometer, using deuterated chloroform or deuterated methanol as the solvent.

Intrinsic viscosities of the polymer samples were determined in a Ubbelohde dilution viscometer (Cannon #50 or #25) mounted in a thermostated (29.5°C) water bath. Efflux times were measured with a digital stopwatch and were recorded to the nearest 0.01 second. Efflux times for H_2O were approximately 105 seconds for the #25 viscometer, and 186 seconds for the #50 viscometer. For each concentration of each solution which was analyzed, at least three measurements were taken, and the average value of the efflux time was used in the calculations (the standard deviation of the measurements was generally +/- 0.1 second).

CHAPTER 3

MACROCYCLIC POLY(2-VINYLPYRIDINE)

Cyclization Reaction-General Considerations

The end-to-end cyclization of P2VP was carried out as described in Chapter 2. Several trial runs were carried out initially, in order to optimize the procedure. Once the procedure had been found to be satisfactory, the relative amounts of 2VP monomer and DD^{-2} initiator were varied in order to obtain polymers having a wide range of molecular weights. In all, over twenty different polymers with molecular weights ranging from 4,000 to over 200,000 were prepared. In each run, a portion of the difunctional living polymeric precursor was isolated and protonated with degassed methanol. This linear precursor was very important to this work, as it allowed SEC determination of the actual molecular weight for each cyclic sample. As will be seen in the following discussion, the size and shape of the polymer coil is changed upon cyclization; however, the molecular weight remains constant, except for the small increase of 104 mass units due to the addition of one molecule of coupling agent. This increase is insignificant, except in the case of very short chains. The linear precursors, in addition to providing an exact molecular weight reference, allow the properties of the cyclic

polymers to be compared to the properties of linear polymers having the same molecular weights.

Size exclusion chrometograms of the crude products from the cyclization reaction (see Figure 14) clearly show the presence of both cyclic polymer and a high molecular weight polycondensate. The yield of cyclic polymer (vs. polycondensate) estimated from the SEC results, ranged from 30 to 70 % (see the section on SEC results). The yield of cyclee generally decreeeed with increasing molacular weight, ee expectad; however, unavoidable small procedural variations from experiment to experiment also had an effect on the yield. Several different experimental approaches were undertaken in order to help maximize the yield. Theoretically, the cyclization yield should be higher when the reaction is carried out at lower temperatures, because the polymer coils are not as expanded (3,14), and the intramolecular reaction should thus be favored. One cyclization experiment was carried out at 0°C by immersing the entire cyclization apparatue in an ice bath. If there was any increase in yield due to the lower temparature, it was barely noticeable and not worth the added degree of experimental difficulty.

It was suggested that by adding an already formed inert linear polymer to the cyclization mixture, the translational motion of the polymer chains in solution could be decreased due to the increased viscosity of the medium. Such an effect should serve to slow the rate of occurrence

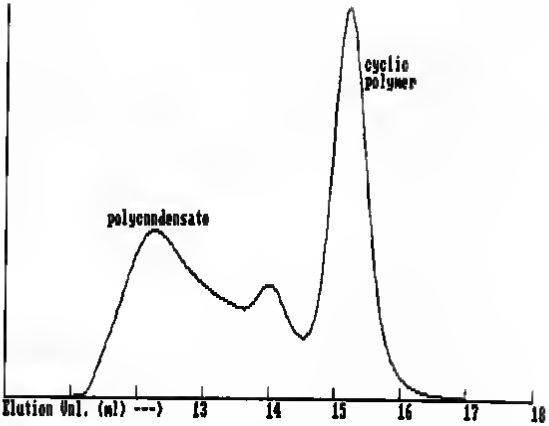


Figure 14. SEC trace of crude product from a typical P2VP cyclization reaction

of the intermolecular reactions and thus increase the cyclization yield. This experiment was carried out by adding 5 grams of polystyrene of molecular weight approximately 200,000 per 100 ml THF in the reaction flask. The cyclization was carried out as before, and the P2VP was separated from the polystyrene by acid/base extraction. No significant increase in cyclization yield was realized. Other workers have attempted to maximize this yield (in the cyclization of polystyrene) by addition of a nonsolvent to the reaction medium (13). There was a slight increase in yield observed, but it was deemed to be not large enough to warrant the added effort. Even though several different approaches could be used to try and maximize the yield of cyclic polymer, no method will give a 100 % yield. For this reason, it will always be necessary to undertake some sort of fractionation procedure in order to obtain samples of cyclic polymer which are free from contamination by polycondensate, therefore, slightly lower yields are acceptable in return for an simpler experimental procedure.

In this work, the method used for the cyclization reaction was to add relatively concentrated solutions ($\sim 10^{-3}$M) of both the living polymer and the coupling agent, dropwise, into a rapidly stirred 500 ml reaction flask containing approximately 250 ml of THF (see Chapter 2). The rates of addition of the two reactants were adjusted so as to always maintain a slight excess ($\sim 10^{-6}$M) of living polymer in the flask. This means that the concentration of

coupling agent in the bulk of the reaction vessel is essentially zero, since the substitution reaction is very fast. In order to verify that the reaction is indeed fast, an experiment was carried out in which a concentrated solution (5×10^{-3}M) of difunctional living P2VP was reacted with a 20% excess of coupling agent (DBX). The two reactants were mixed quickly at room temperature, and the red color of the living polymer was seen to disappear in the time required for mixing of the two solutions (about one or two seconds). This corresponds to a minimum rate constant greater than 5×10^3 l mol^{-1}s^{-1} for the cyclization reaction. Now consider the situation at the point where the droplets of living polymer solution are entering the reaction solution. The relatively concentrated droplets of living polymer solution are entering a solution which already contains an excess of living polymer. This leads to a region which has a localized higher concentration of living ends, but this is quickly dissipated by the rapid stirring. This local excess of living ends has no significant effect on the course of the reaction, since the concentration of coupling agent at this point is virtually zero, due to the large rate constant of the reaction and the fact that the living polymer is in excess. The situation at the other side of the flask, where the coupling agent is being added, is more critical because the localized concentration of coupling agent exceeds that of the living polymer, before being dissipated by stirring.

This small volume element of the solution is undoubtedly where most of the reaction takes place, and the local excess of coupling agent in this area is probably responsible for the formation of most of the polycondensate. The effect can be minimized by making the coupling agent solution more dilute and/or by making the drops as small as possible. Indeed, it was found that better yields were obtained by using a more dilute coupling agent solution; however, this aspect of the reaction was not studied quantitatively. It should be noted that there are three distinct advantages to keeping the living polymer, rather than the coupling agent, in excess during the reaction. First, the intense red color of the living polymer makes it easy to monitor the concentration visually. Second, a localized excess of coupling agent should be be more quickly dispersed than will a localized excess of polymer, due to the higher viscosity of the polymer solution. Finally, this method allows the living polymer solution which is being added to be of a higher concentration, since a local excess of living polymer will be dispersed by stirring, before any appreciable reaction takes place (due to the extremely low concentration of coupling agent in the bulk of the solution; see above). A living polymer feed solution having a higher carbanion concentration is advantageous because such a solution will experience less deactivating side reactions prior to use, due to its lower proportion of free ions (27).

The method described above is different from the methods other groups have used for the preparation of cyclic polymers by end-to-end coupling. Roovers and Toporowski's (10) method involves successive additions of 1 to 2 milliliter aliquots of living polymer solution followed by slow addition of coupling agent. This process is repeated many times. The method used in the present work is essentially continuous and is equivalent to hundreds of small successive additions (drops), rather than dozens of larger ones. This allows a lower overall concentration of living ends to be maintained in the reaction flask, without large concentration fluctuations. Rempp et al. (28), in their later work, used the same method as did Roovers; however, in Rempp's earlier work (13,29), as well as in the experiments of Vollmert and Huang (12), the cyclization was carried out by repeated successive additions of precise amounts of initiator, monomer, and then coupling agent. This later method suffers from the drawback that it may be very difficult to add precisely the same amount of each reagent each time, and such variations may lead to a broader MWD. In addition to the present method allowing a more uniform addition of reagents, it is also very simple and requires less manipulation than the other methods. While it is possible that some improvements can be made, it is clearly the most convenient method developed to date, and gives excellent results.

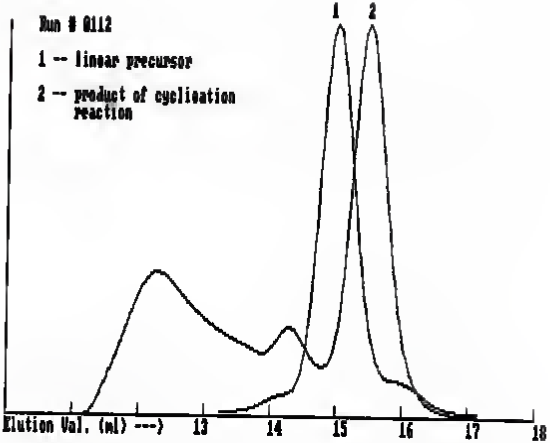


Figure 15. Comparison of SEC traces of a crude cyclization product with its linear precursor

In Figure 15, the SEC trace of the crude product from a typical cyclization experiment is compared with that of the linear precursor for that experiment. Two important facts are readily apparent. First, the elution volume of the main peak of the cyclization product is higher than that of the original polymer. This indicates that the product has a smaller hydrodynamic volume than the precursor. Second, the width of the shifted peak is almost exactly equal to the width of the precursor peak. Both of these facts are consistent with the formation of a cyclic polymer. In addition to being predicted theoretically (30,31), and proven experimentally (2,7,10-13), one might expect intuitively, that by placing an end-linking constraint on a polymer chain, the average dimensions of that chain in solution should decrease. Both the decrease in hydrodynamic volume and the narrow molecular weight distribution of the coupled product constitute substantial evidence for the formation of cyclic polymer. Since the polymer has a narrow molecular weight distribution to begin with, it seems reasonable that the average dimensions of each chain should decrease by the same proportion upon cyclization. This means that a perfectly cyclized sample should have a MWD which is equal to that of the linear precursor. Since the widths of the two peaks shown in Figure 15 are equal, the two polymers (cyclic and linear) can be considered to have equal MWD's. This is very good evidence that the cyclic product is not contaminated by any

significant amount of linear polymer. In fact this was the criterion used in determining whether or not a given run was suitable for inclusion in this study. Occasionally, due to the sensitive nature of the cyclization reaction, a product was significantly contaminated by linear material (usually caused by a small pinhole in the glassware), as evidenced by a SEC peak much broader than that of the precursor. Such samples were discarded.

The various possible reactions involving a difunctional living polymer and a difunctional coupling agent have already been illustrated in Figure 4. Assuming exact stoichiometric amounts of both, and the absence of accidental termination reactions, only cyclic products having integral multiples of the precursor molecular weight should be formed. If however, some of the polymer chains become terminated on one end, or were generated from initiator molecules which had been prematurely deactivated on one end, then they must necessarily couple with other chains (they cannot cyclize), and continue to do so, until either they couple with another monofunctional chain, or become deactivated through side reactions or reactions with impurities. As long as impurities are rigorously excluded from the system, and the percentage of one-ended chains is small to begin with, any linear polycondensate formed should be of a very high molecular weight, because the probability of two one-ended chains reacting with each other is much less than the probability of a one-ended

chain reacting with a difunctional chain to give a longer one-ended chain. It is instructive to consider some numerical examples in order to examine the effect which small amounts of premature termination have on the structural integrity of the cyclic polymers. Consider first a living polymer sample (of molecular weight M) which is 100% difunctional at the end of the polymerization reaction and before the addition of any coupling agent. Now consider the effect of protonating 10% of all the living ends in the system. The probability that a given chain end is protonated is thus (0.10), and the probability that a given polymer chain will have both of its ends deactivated is (0.01). This means that only one percent of the chains in the sample will be unable to undergo either cyclization or coupling and thus end up as a linear contaminant in the fractionated cyclic polymer. Of the 99% of the original chains which are still active, 82% are difunctional and 18% are terminated at one end only. The probability for a one-ended chain to couple directly with another one-ended chain is thus (0.18 x 0.18)=(0.032), whereas the probability for a one-ended chain to react with a difunctional chain is (0.18x 0.82x2)=(0.30). Thus, only (0.032/ 0.032+0.30) =(9.6%) of the one-ended chains will couple directly with other one-ended chains. This amounts to only (9.6% x 18%) =(1.7%) of the total number of original chains in the system, and even so, these coupled linear chains now have a molecular weight 2M (double that of the original polymer)

so they do not affect the structural integrity of the fractionated cyclic product, as they are removed with the rest of the polycondensate. Now consider a similar case, where the deactivation occurs on the initiator, before the polymerization. Using the above reasoning, one percent of the initiator molecules will be deactivated on both ends. These terminated initiator molecules do not affect the structural integrity of the product since they are of very low molecular weight. This leaves a mixture 82% difunctional initiator and 18% monofunctional initiator. Assuming that no deactivation occurs during the polymerization reaction, the chains which grow from the monofunctional initiator will be expected to have a molecular weight one-half that of the chains which grow from the difunctional initiator. By following the above reasoning, it can be seen that approximately 10% of these one-ended chains will couple with each other to form some terminated linear polymer with a molecular weight equal to that of the polymer formed from the difunctional initiator. This makes up less than one percent by weight of the total polymer in the system. The remaining 90% of these short one-ended chains will be incorporated into the polycondensate. Even if the cyclization yield in this case were only 30%, this would only amount to about 3% linear contamination in the fractionated cyclic product. This amount is amazingly small, considering that almost one-fifth of the initiator molecules were partially deactivated. These examples

illustrate that in the absence of major amounts of accidental deactivation of the living ends, the structural integrity of the cyclic polymers can be expected to be very high. Also, since the proportion of one-ended chains in the reaction mixture is very small to begin with (less than five percent, even in the worst cases), it is expected that the polycondensate will contain primarily cyclic molecules. A further discussion of this point will be presented at the end of this chapter.

Some of the linear precursors which were used exhibited high and/or low molecular weight shoulders in their SEC traces (see Figure 15). The low molecular weight shoulder, with a molecular weight of approximately one-half that of the main peak, is due to one-ended polymer formed from initiator which was partially deactivated before addition of the monomer. This amounted to no more than a few percent of the total material, and does not lead to any significant contamination of the cyclic product by linear material (as explained above). The high molecular weight shoulder observed in some cases was found to be a result of side reactions caused by letting the living polymer solutions sit at room temperature for extended times (longer than a few minutes). These side reactions were investigated in some detail and it was determined that the high molecular weight shoulder in the SEC was caused by a coupling reaction involving the living chain ends. These reactions are quite interesting in themselves and will be

discussed in detail in Chapter 6. These side reactions are not believed to have had any detrimental effects on the cyclization reaction, but nevertheless, efforts were made to keep the living polymer solutions at -78°C until the cyclization reaction was carried out.

Two other important aspects of the cyclization reaction bear mentioning here. The formation of catenated rings (rings which are physically interlocked with, but not covalently bonded to other rings) cannot be overlooked (see Figure 16). Such species must necessarily form, and their yield should increase with increasing molecular weight. The yield of catenated rings should also increase in the later stages of the cyclization reaction, when the concentration of already formed rings, and hence the number of chain entanglements, is higher. The presence of such structures is very hard to prove, as they would be contained in (and obscured by) the rest of the polycondensate. Such species are not of major importance in the present work, because they are removed in the fractionation procedure. The formation of catenated rings has been discussed by several authors (10,12); but they have not been studied in the present work.

Another interesting aspect of the cyclization reaction which bears mention is the possibility of the formation of permanent knots in the cyclic polymer chains (see Figure 16). Transient knots can be formed in any linear polymer chain, but upon cyclization, such knots are made permanent.

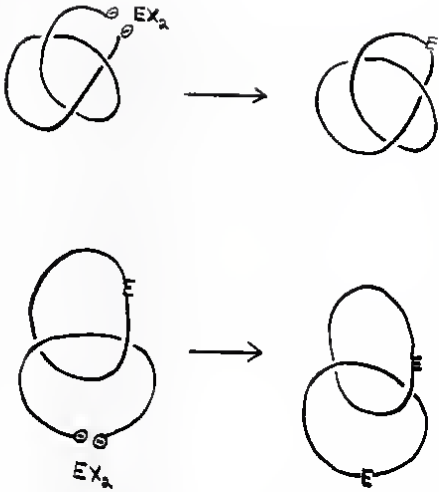


Figure 16. Formation of knotted polymer (top), and catenated polymer (bottom), during an end-to-end cyclization reaction

Several authors have addressed this possibility (10,32,33). Roovers (10) concluded that for polystyrenes of molecular weight less then a few hundred thousand, the probability for the formation of knots is very small, particularly when the cyclization is carried out in a thermodynamically good solvent.

In order to separate the cyclic polymer from the polycondensate, the crude cyclic products were fractionated according to the procedure given in Chapter 2. In this manner, cyclic samples with MWD's comparable to those of the linear precursors were obtained. In some cases, a few percent of polycondensate remained in the fractionated samples of cyclic polymer. This was sometimes necessary in order to obtain larger amounts of material, as there is a trade-off between purity and yield. In Figure 17, an SEC trace of a typical fractionated cyclic polymer is compared to that of the crude cyclization product from which it was obtained.

SEC Results

All fractionated cyclic samples and linear precursors were analyzed by SEC at room temperature using THF containing one percent triethylamine as the mobile phase. The results are compiled in Table 1. The cyclization yield for each run was estimated from the SEC chromatograms of the crude products. These yields ranged from approximately thirty to seventy percent, with the higher yields being obtained in the lower molecular weight runs. The molecular

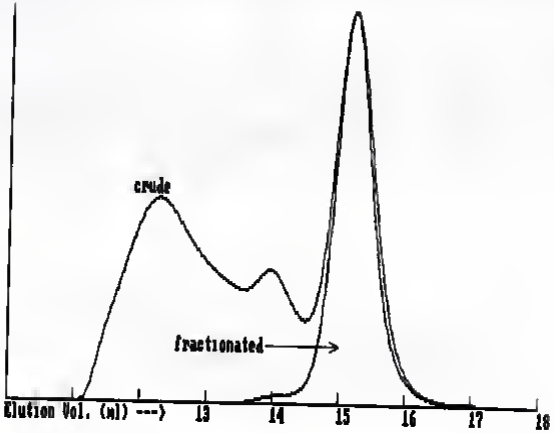


Figure 17. Comparison of SEC traces of fractionated cyclic P2VP and crude cyclization product

Table 1. SEC DATA FOR CYCLIC P2VP

RUN #	YIELD[a]	M_p(L)[b]	(M_w/M_n)	M_p(C)[b]	(M_w/M_n)	<G>[c]
0728	70%	4,010	(1.06)	3,390	(--)	.85
0521	60%	5,240	(1.06)	4,370	(1.16)	.83
1030	50%	10,700	(1.06)	8,340	(1.08)	.78
0414	65%	11,200	(1.04)	8,820	(1.04)	.79
0630	50%	14,600	(1.04)	11,400	(1.05)	.78
1011	50%	15,500	(1.09)	12,200	(1.10)	.79
0112	55%	23,600	(1.06)	17,800	(1.04)	.75
0209	65%	24,000	(1.05)	18,300	(1.10)	.77
0720	50%	24,600	(1.06)	18,800	(1.09)	.76
0707	50%	25,000	(1.06)	18,800	(1.06)	.76
0716	45%	25,300	(1.06)	19,400	(1.07)	.77
0729	55%	25,600	(1.06)	19,700	(1.12)	.77
0102	45%	26,800	(1.07)	20,200	(1.04)	.75
0121	40%	29,200	(1.06)	22,600	(1.04)	.77
0217	50%	60,300	(1.08)	44,300	(1.08)	.74
0223	45%	63,600	(1.11)	47,700	(1.13)	.75
0225	40%	112,000	(1.14)	83,600	(1.15)	.74

a. approximate cyclization yield estimated from SEC chromatogram of crude cyclization product

b. SEC peak molecular weight for linear precursor (L), and fractioneted cyclic polymer (C) (based on calibration with linear standards) (+/- 1.5% - see chapter 3)

c. ratio of M_p(C) to M_p(L) (+/- .02; see chapter 3)

weights listed for the cyclic polymers are apparent molecular weights based upon calibration with linear P2VP standards. In all cases these values are lower than the actual values, which are represented by the molecular weights of the linear precursors.

In addition to the samples listed in Table 1, a cyclization experiment was carried out using a linear precursor of molecular weight 240,000. The cyclization yield in this case was approximately 30%. The SEC analysis of the crude cyclization product revealed that the decrease in hydrodynamic volume in this case was at least as great as for the samples listed in Table 1. For unknown reasons, the fractionated cyclic sample, after several months of storage, exhibited strong adsorption onto the SEC column, and therefore could not be accurately analyzed. For this reason, the results for this sample were not included in Table 1. Dilute solution viscosity and DSC measurements on this sample revealed no peculiarities, and the results of these experiments were consistent with the formation of a cyclic polymer.

The ratio of the peak molecular weights for each cyclic/linear pair in Table 1 is denoted by <G>. It can be seen that the values of <G> decrease with increasing molecular weight. These values range from 0.645 to 0.736 over the molecular weight range of 4,010 to 112,000, and are seen to generally decrease with increasing molecular weight. The molecular weight distributions for the

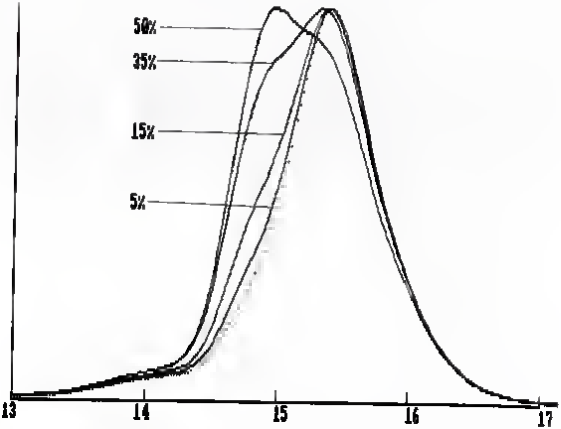


Figure 18. SEC traces of solutions of cyclic P2VP which contain the indicated percentages of added linear precursor
(dotted line is "pure" cyclic P2VP)

fractionated cyclic polymers are also listed, and in most cases are comparable to those of the corresponding linear precursors.

As mentioned above, the cyclic samples exhibited narrow SEC peaks with widths identical to those of the precursors. This was taken as good evidence for the absence of significant contamination of the cyclic polymers by linear chains. In order to test this assumption, small amounts of linear precursor were added to a fractionated cyclic sample (sample # 0720CF). Such mixtures were analyzed by SEC and it was found that noticeable peak broadening occured, even for samples containing less than 5% added linear polymer. The SEC traces for a cyclic P2VP fraction containing various amounts of added linear precursor are shown in Figure 18. These results confirm that the cyclic samples are indeed very low in linear polymer content. Such a result is not surprising, since for reasons discussed above, the cyclization reaction does not lend itself to the formation of low molecular weight linear material in any significant quantities, as long as the occurence of deactivating side reactions is minimal. It should be pointed out that such side reactions are much less likely to occur in the P2VP system than in the polystyrene system (4), so the cyclic polymers of P2VP may be expected to have a higher degree of structural integrity than those of polystyrene.

Viscosity Results

Both the SEC elution volume and the intrinsic viscosity, $[\eta]$ of a macromolecule in solution are related to the hydrodynamic volume of the molecule. Molecular weight and intrinsic viscosity are related to each other through the well-known Mark-Houwink relationship which is given in Equation II:

$$[\eta] = K \cdot M^{a} \qquad (II)$$

Intrinsic viscosities were measured for the cyclic and linear P2VP samples. In order to make more accurate comparisons between the SEC and viscosity data, the viscosities were determined in the same solvent (THF + 1% Et_3N) as was used for the SEC measurements. The intrinsic viscosities were determined by extrapolating plots of reduced viscosity vs. concentration to zero concentration. Such a plot for one typical cyclic/linear pair is shown in Figure 19. Since these plots were found to have slopes which were very close to zero, values of the reduced viscosity at C = 0.100 g/dL were taken to be equal to the intrinsic viscosity in some cases. Since the slope of such plots is known to be an increasing function of the intrinsic viscosity (14), and hence of molecular weight, the error introduced by making this assumption should be greater for the high molecular weight samples. Even for the highest molecular weight samples though, the slopes were very small and the assumption is thus justified.

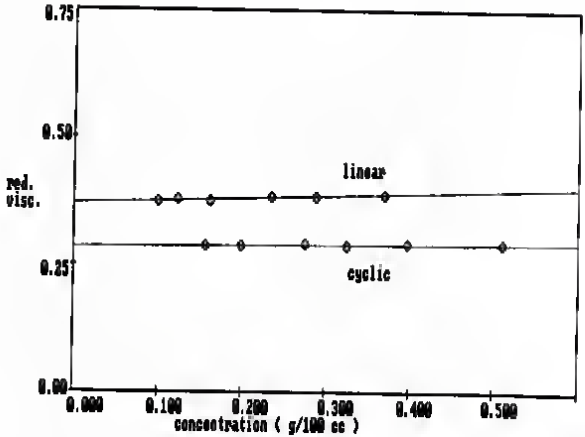


Figure 19. Plot of reduced viscosity (THF, 29.5°C) vs concentration for a cyclic/linear P2VP pair (MW = 117,000)

On the basis of the Mark-Houwink relationship, it is expected that the ratio of intrinsic viscosities of cyclic and linear P2VP samples having the same molecular weight (denoted by <g'>), should be less than one, and exhibit the same decrease with increasing molecular weight that is seen for the values of <G>. This trend is very evident in the Mark-Houwink plots (Ln M vs. Ln [η]) of cyclic and linear P2VP (see Figure 20). Values for several narrow MWD commercial linear P2VP standards are included in the plot for the linear polymers. The slopes of these two plots ("a" in Equation II) were determined by linear regression analysis. The value of "a" for linear P2VP was found to be 0.66 (+/-.02), while the value for cyclic P2VP was found to be 0.58 (+/-.02). The value for linear P2VP exactly matches that determined by Mencer and Grubisic-Gallot (25) for linear P2VP in THF at 25°C. The finding of a smaller slope for the cyclic polymers simply restates the fact that the value <g'> decreases with increasing molecular weight. From these plots, values of <g'> at any given molecular weight can be determined, with <g'> increasig from 0.66 at molecular weight 200,000 to 0.88 at molecular weight 5,000. These graphically determined values of <g'> are more representative of the actual trends than are the individually determined points, because there is some scatter to the points and the graphically determined values reflect an average over all the samples. The SEC results

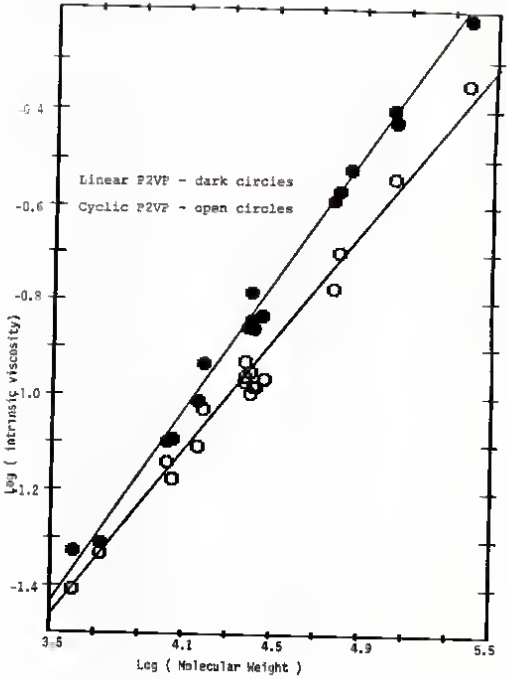


Figure 20. Mark-Houwink plots for cyclic and linear P2VP (THF / 1% Et_3N, 29.5°C)

probably give a more accurate reflection of the actual size of the "pure" cyclic and linear polymer molecules than does the viscosity data, because the peak molecular weights determined by SEC are rather well-defined values which reflect the hydrodynamic volume of the species present at the peak maximum, and they are not significantly affected by the presence of small amounts of high or low molecular weight impurities, or errors in the concentration of the solutions being analyzed. Intrinsic viscosity measurements, on the other hand, reflect an average of the whole sample, including any high or low molecular weight impurities which may be present. They are also extremely sensitive to errors in concentration and dilution of the solutions being analyzed.

A Mark-Houwink exponent which is lower for cyclic P2VP than for linear P2VP indicates that as molecular weight increases, the cyclic polymers expand to a lesser degree than do the linear polymers. It should be pointed out that the experimentally determined values of the Mark-Houwink exponent are greater than 0.5, indicating that THF is a thermodynamically good solvent for P2VP at the temperature of these measurements (29.5°C), and that it is a slightly better solvent for linear than for cyclic P2VP.

Following the treatment of Jordan and McConnell (34), it is possible to derive a theoretical relationship between <G> and <g'>. This relationship is given by Equation III.

$$\langle G \rangle = \langle g' \rangle^{1/(1+a)} \qquad \text{(III)}$$

where "a" is the Mark-Houwink constant for the linear polymer. The values of <G> calculated from Equation III, using values of <g'> determined graphically from Figure 20, range from 0.78 at a molecular weight of 200,000, to 0.93 at a molecular weight of 5,000. These values are slightly higher than the corresponding values of <G> determined experimentally (see Table I). As discussed above, the viscosity measurements reflect an average of the entire sample, whereas the SEC peak molecular weights are rather well-defined values describing the hydrodynamic volume of the species present at the peak maximum. It seems very unlikely that the magnitude of the differences between cyclic and linear polymers of the same molecular weight could be overestimated by either method; therefore, the differences as determined by the SEC measurements are probably more representative of the actual differences in the hydrodynamic volumes of the "pure" cyclic and linear polymers. The ratios of the intrinsic viscosities of cyclic and linear polymers of the same molecular weight could be overestimated due to the fact that some of the linear samples contained a few percent of low molecular weight material, which would tend to decrease the measured viscosities; and a few percent of the polycondensate remains in some of the cyclic samples, tending to make these viscosities higher. Neither of these types of impurities would have an effect on the SEC peak maximum. If the

opposite approach is used (where <g'> is calculated using experimentaly determined values of <G>), then a range of <g'> from 0.82 to 0.55 (from molecular weights 5000 to 100,000, respectively) is predicted. Such a range is in very good agreement with values reported for polystyrene in a good solvent (11). Contamination of the cyclic samples by linear polymer would also give measured values of <g'> which are higher than predicted theoretically, but based upon the SEC data, this can be ruled as the cause of the discrepancy. Eventually, these discrepancies will be resolved by other independent measurements of hydrodynamic volume (such as light-scattering). Such measurements are currently being carried out.

The SEC and intrinsic viscosity data clearly show the same basic trends, both indicating that a cyclic P2VP molecule in solution is smaller (more compact) than a linear P2VP chain having the same number of segments, and that the cyclic and linear polymers tend to become closer in size as the lengths of the chains become less. The first point is not suprising, because as mentioned previously, this has been observed in other polymer systems (2,10-13), and has been predicted theoretically (30,31). The fact that the two polymers become closer in size as the molecular weight decreases is not readily apparent, and a more detailed explanation is required in order to better understand its cause and significance. Several groups (11,35)

have found that in thermodynamically good solvents, the ratios of the hydrodynamic volumes of cyclic and linear polystyrenes tend to decrease with increasing molecular weight. This is in good agreement with the results reported here for P2VP, and such behavior has been predicted theoretically by Bloomfield and Zimm (36). Other theories (37,38) have predicted the opposite behavior; however these theories have not been supported by any experimental results to date. Data indicating that <g'> and/or <G> (for polystyrene in a good solvent) either remain constant or increase with increasing molecular weight have been reported (13,29), but such findings have been shown to have been caused by the presence of linear contamination in the higher molecular weight cyclic samples (28). Since the bulk of the published data on cyclic polymers agrees with the results for P2VP presented here, any results for similar polymers which predict the opposite behavior should be suspect.

A cyclic chain of a given length occupies a smaller volume in solution than does a linear chain having the same number of units. This means that the cyclic chain must necessarily have a greater average segment density than the linear chain. Because of this higher segment density, a cyclic chain must be subject to more long-range intramolecular non-bonded interactions than the linear chain is. It is well known, but unexpected, that for a random-walk

linear coil, the segment density at the center of mass increases as the chain becomes shorter (14). This same effect should also hold for cyclic polymers, therefore, as a cyclic chain is made shorter, the intramolecular non-bonded interactions (which are greater than in the linear chain to begin with), should become even more important. This effect may serve to prevent a cyclic chain from being able to collapse to the same extent as a linear chain when the length of the chain decreases, and thus the dimensions of the cyclic chain will approach those of the linear chain. Placing an end-linking constraint on a polymer chain also decreases the number of possible conformations available to the chain. As the chain becomes shorter, this constraint results in a stiffer chain. This inherent stiffness may serve to keep small cyclic chains "puffed-up" relative to the more flexible linear chains of the same length. Similar behavior has been observed for comb-branched polymers (39), which also have a higher segment density and a lower number of possible configurations than do linear polymers with the same number of units. These effects, in addition to playing an important role in determining the solution properties of cyclic macromolecules, may also be very important in determining their bulk properties as well.

The effect of the presence of a coupling agent in the cyclic macromolecules cannot be ignored. While its effect

in very long chains should certainly be negligible, it may play an important role in determining the behavior of very small cyclic polymers. The coupling agent results in a para-xylyl group ($-CH_2-Ph-CH_2-$) being incorporated into the polymer backbone. The presence of such a group results in an increase of 104 mass units in the molecular weight of the chain, but this effect is rather small. Although the size of the coupling agent moiety is approximately equal to that of one monomer unit, the contribution it makes to the contour length of the chain is much greater, owing to the rigid 1,4- linkage at the phenyl ring. Not only does the coupling agent add to the overall length of the cyclic chain, but it is also inflexible and thus contributes an added degree of stiffness to the chain. Such effects due to the coupling agent must certainly exist, and no doubt are responsible for part of the observed behavior, particularly for the shortest chains studied; however, the changes in the ratios of the hydrodynamic volumes of the chains continue to be observed (although to a seemingly lesser extent) even at higher molecular weights, where the effect of the coupling agent should be minimal. It seems likely; therefore, that the observed divergence of the relative dimensions of cyclic and linear P2VP is caused by a combination of the effects of intramolecular excluded volume and the presence of the coupling agent. In order to fully understand the effect that the coupling agent has on the

cyclic chain, it will be necessary to study the properties of cyclic polymers prepared using a more flexible, or smaller coupling agent (such as the ortho-substituted bis(chloromethyl)benzene).

Glass Transition Temperatures

The linear and fractionated cyclic P2VP samples were analyzed by differential scanning calorimetry (DSC). The methodology used in these studies has been described in detail in Chapter 2. The polymers were studied in the temperature range of 50°C to 100°C. All of the samples exhibited a glass transition, characteristic of amorphous polymers. No sign of crystallinity, as evidenced by a melting peak in the DSC curve, was observed for any of the samples. As the glass transition temperature (T_g) is approached, the polymers begin to soften, and at higher temperatures they begin to behave like viscous fluids. This type of behavior is actually quite different than the sharp melting point which crystalline polymers show. In terms of the entropy theory of glasses, the glass transition temperature is defined as the point where the configurational entropy reaches a critical value (40). In molecular terms, the glass transition temperature can be defined as the temperature at which major portions of the polymer chain begin to show significant segmental motion as the temperature is raised (3). This means that portions of the chain have enough energy to overcome the barriers to

torsional rotation, and hence segments of the chain begin to move due to rotation around consecutive bonds in the polymer backbone. Below the glass transition temperature, all segments of the polymer chain are essentially fixed in position with respect to neighboring segments (intra- or intermolecular). Above the glass transition temperature, the chains acquire additional energy and eventually whole chains obtain complete translational motion and can move with respect to each other. When this happens, the polymer behaves like a liquid. It should be pointed out that the glass transition temperature is not an exact and well-defined point, but rather a temperature describing the midpoint of the temperature range over which the transition occurs. Chain ends play a very important role in the glass transition of a polymer. It is well known that low molecular weight linear polymers exhibit a sharp increase in T_g as molecular weight is increased. Since the energy barrier to rotation about the backbone is much lower at the end of a chain than it is in the center of a chain, it is the chain ends which gain significant segmental motion first. As the length of a chain becomes greater, the effect of the chain ends becomes negligible, and the T_g asymptotically approaches a limiting value.

Glass transition temperatures were determined from the DSC curves of all the cyclic and linear P2VP samples. The T_g values are plotted against molecular weight in Figure

21 It can be seen that the T_g's of the cyclic P2VP samples are higher than for their linear homologues. The difference is greatest at low molecular weights, with the T_g's of the cycles decreasing as chain length increases. The T_g's of the linear P2VP increase with molecular weight, as expected for linear polymers. The two curves tend to converge at a molecular weight of about 60,000, approaching a limiting value of approximately 100°C. At the lowest molecular weight studied (~4000), the difference in the T_g's is approximately 32°C. Although no quantitative estimate of the structural integrity of the cyclic samples can be made based on the T_g data, the extreme differences observed for cyclic and linear polymers suggest that the structural integrity, at least for the smaller rings, is indeed quite high. Similar results have been reported (2,41) for cyclic and linear poly(dimethylsiloxane) (PDMS). The P2VP results are also very similar, at least qualitatively, to recently published theoretical predictions of the relationship between molecular weight and T_g for cyclic polystyrene and cyclic PDMS (42). In both cases, these predictions, which are based on configurational entropy calculations, predict that the T_g's should be higher for cyclic polymers than for linear polymers, and that the T_g's of cyclic polymers should decrease with increasing molecular weight. It should be pointed out that the experimental results for PDMS agree very nicely with

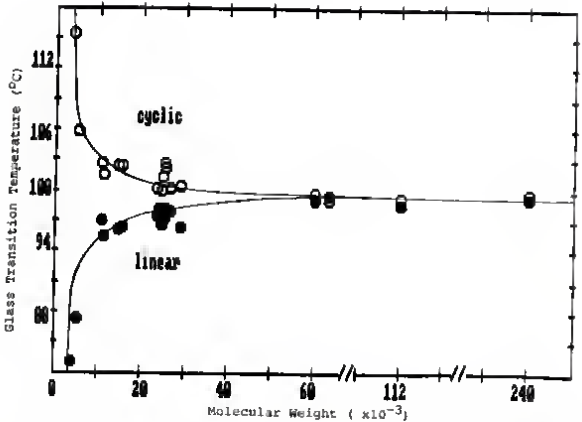


Figure 21 Plot of glass transition temperature vs. molecular weight for cyclic and linear P2VP

these theoretical predictions. Since the structures of polystyrene and P2VP are very similar, it is expected that the relationship between T_g and molecular weight for these two polymers should be similar. In fact, the T_g of high molecular weight linear polystyrene is approximately 100°C, almost exactly the same as for high molecular weight P2VP. One study (43) of the T_g vs. molecular weight behavior of macrocyclic polystyrene has reported that the T_g's of low molecular weight cyclic polystyrenes are higher than those of linear polystyrenes of the same molecular weights. This difference is greatest at the lowest molecular weights, and becomes less as molecular weight increases, but in contrast to the results for P2VP, the T_g's of the cyclic polystyrenes are reported to increase, rather than decrease with increasing chain length. The values for the cyclic polystyrenes asymptotically approach the same limiting high molecular weight value (~100°C) as do the linear polystyrenes, only they do so at a lower molecular weight. It appears that the same effects may be at work in both the polystyrene and the P2VP systems, but that the effects are much more pronounced in the P2VP system. It is possible that the continuous increase in T_g with increasing molecular weight observed for the cyclic polystyrenes is due to the presence of significant amounts of linear material, but there is no proof of this. The lower than expected T_g's could also be due to the fact that Me_2SiCl_2 was used as the coupling agent in this polystyrene system (see below).

In order to investigate the effect of the presence of linear chains on the T_g of cyclic P2VP, mixtures containing various proportions of cyclic and linear P2VP were made homogeneous by dissolving the mixtures in $CHCl_3$ and then reprecipitating them in hexane. The lowest molecular weight sample (MW - 4000) was used in this study, because this sample showed the greatest T_g difference between the cyclic and linear polymers. The T_g's of such mixtures were determined and are plotted against composition in Figure 22, along with the values for the pure cyclic and linear polymers. A linear relationship between composition and T_g is observed, indicating complete compatibility for the cyclic and linear P2VP.

The observed difference in glass transition temperatures for cyclic and linear P2VP seems to be the result of two different factors. It has been shown that chain ends play a very important role in determining the glass transition temperature of low molecular weight polymers. For very long linear chains, where the chain ends make up an insignificant proportion of the total volume of the polymer sample, no increase in T_g is seen with a further increase in molecular weight. In fact, it has been shown that highly-branched comb-type polystyrenes (which contain a much higher proportion of chain ends than do linear polymers of the same molecular weight) can have T_g's lower than those of linear polystyrenes with the same number of units

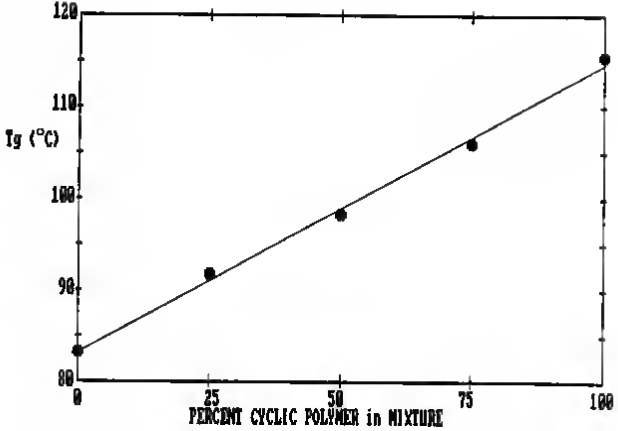


Figure 22. Glass transition temperature vs. composition for mixtures of cyclic and linear P2VP (MW = 4,010)

(39). Since cyclic polymers contain no chain ends, one might expect that the T_g for a cyclic polymer would be very close to the value for a long chain linear polymer, and not be dependent on molecular weight. The absence of chain ends is no doubt responsible for a significant part of the observed behavior; however, if this were the only factor at work, then the T_g of the cyclic polymers would be expected to be constant, not increase, as chain length decreases. The T_g's of high molecular weight cyclic and linear polymers are seen to be equal. Semlyen (41) attributes this to the fact that the same local conformational statistics apply to both cyclic and linear molecules at infinite molecular weight. As discussed above, the stiffness of a cyclic chain increases as molecular weight decreases, because of the lower number of possible configurations which result from the end-linking constraint. A more rigid chain, by definition, implies a higher barrier to torsional rotation, and a lower configurational entropy; thus, a higher temperature is necessary to permit segmental motion. Since the rigidity of the cyclic chain decreases with increasing chain length, the T_g is expected to decrease as chain length increases. This two-part explanation (absence of chain ends and increased chain stiffness in the cyclic polymers) serves to explain the results for P2VP quite well. In the discussion of the solution properties of cyclic P2VP, it was suggested that the coupling

agent adds a degree of stiffness to the polymer chains. This effect should become more pronounced as the chains become shorter, and could certainly lead to results like those seen here. It is not likely however, that this effect alone is responsible for the observation that the T_g of cyclic P2VP increases with increasing molecular weight, because a similar trend is seen for cyclic PDMS (42), which contains no such rigid coupling agent. The interesting observation that the T_g's of low molecular weight cyclic and linear P2VP differ by a significant amount suggests that the presence of cyclic polymer in a sample can be verified by DSC measurements. It was suggested above, that the polycondensate produced during the cyclization reaction contains a significant amount of cyclic polymer having integral multiples of the precursor molecular weight. In order to ascertain whether this is indeed the case, the polycondensate from sample # 0521 (MW ~ 5,000) was fractionated to obtain a sample which by SEC analysis was estimated to contain mostly material consisting of three or four chains linked together. The apparent molecular weight (SEC) of this material was approximately 18,000 (M_w/M_n = 1.25), but the actual molecular weight would be higher if the sample contained any significant amounts of cyclic material. Care was taken during the fractionation procedure to ensure that virtually all of the "monomeric" cyclic polymer was removed. The polycondensate sample was

analyzed by DSC, and it was found that the observed T_g was substantially higher (~6°C) than that of pure linear P2VP of molecular weight 18,000, and even slightly higher than the corresponding cyclic P2VP. This result indicates that at least part (or even most) of the polycondensate is cyclic in nature. The measured T_g is a little higher than is expected from a pure cyclic sample of molecular weight 18,000, but this can be accounted for by considering that the polycondensate sample also contains a small amount of cycles which have a lower molecular weight which were not removed by the fractionation (it also contains some cycles of higher molecular weight, but these have no appreciable effect on the T_g). Further evidence for the formation of cycles of higher molecular weight can be seen in the SEC traces of the crude products from the cyclization reaction. Most of these chromatograms contain three distinct peaks (see Figure 23). The lowest molecular weight peak (~50% of the total material) is very sharp and is comprised of "monomeric" cyclic material. The highest molecular weight peak (~40%) is rather broad and consists of very high molecular weight material (more than three chains linked together). In most cases an intermediate, relatively sharp peak (~10%) is observed. This middle peak falls very close to the elution volume expected for material having double the precursor molecular weight, but it is shifted to an elution volume slightly higher than is expected for a

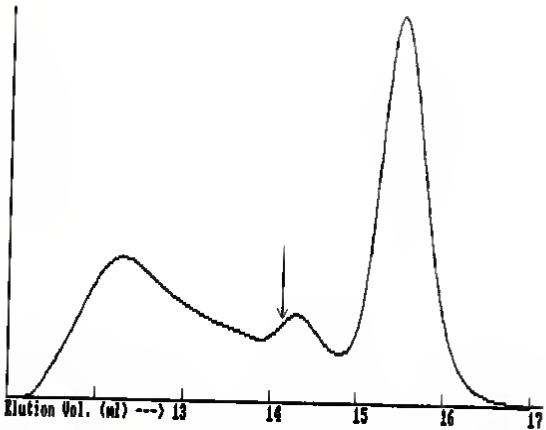


Figure 23. SEC trace of a crude cyclization product, showing expected elution volume for a linear polymer having double the precursor molecular weight

linear dimer. This fact, along with the high T_g observed for the polycondensate, confirms the presence of cycles having molecular weights several times higher than that of the linear precursor.

CHAPTER 4

QUATERNIZATION OF CYCLIC AND LINEAR P2VP

General Considerations

It is well known that poly(vinylpyridines) can be quaternized with alkylating agents in order to convert them into water-soluble polyelectrolytes (6). Fuoss and Mealay (44) have reported the quaternization of P2VP using both n-butyl bromide and methyl bromide in nitromethane. The reaction with butyl bromide was reported to result in quaternization of approximately 50 % of the pyridine units vs. approximately 66 % for the reaction with methyl bromide. Similar studies using poly(4-vinylpyridine) indicate that greater than 95 % reaction can be achieved, even with the larger butyl bromide (45). Reactions of this type are illustrated in Figure 24. The incomplete reaction in the case of P2VP is believed to be due to a combination of steric interactions of the alkyl group with the chain, and electrostatic effects which result from the placement of additional positive charge on a positively charged chain (44,45). Complete quaternization is not necessary in order to obtain polymers which are completely water soluble; although, polymers with a higher degree of quaternization are expected to have higher solution viscosities in water. These types of polymers are reported to show an

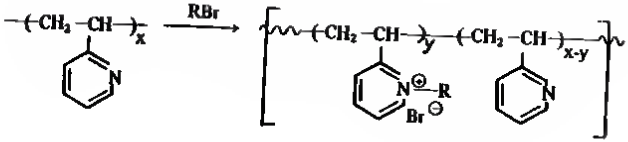


Figure 24. Quaternization of P2VP with an alkyl halide to give a polyelectrolyte

increase in reduced viscosity upon dilution in H_2O (14,44,46). Such behavior is typical for polyelectroiytes, and can be explained by considering what happens when a poiyelectroiyte solution is diluted. At relatively high concentrations (~1% w/v) the poiymer molecuies in soiution partiaiiy overiap each other, and the solution is essentiaiiy homogeneous. As the eolution is diluted, the separation between polymer molecules becomes greater. The counter-ions, being mobiie, can diffuse into the intervening soiution, thua causing a net buildup of charge in the poiymer domain. This ieads to an increase in electrostatic repuision between the fixed charges and a subsequent expansion of the polymer chain. Apparently, the literature contains no reports of the synthesis of macrocyciic polyelectrolytes.

Quaternization Reaction

Cyclic and linear P2VP were quaternized according to the procedure outiined in Chapter 2. The resuits of these quaternization reactions are summarized in Tables 2 and 3. Various aikyi haiides (CH_3Br, CH_3I, and CH_3CH_2Br) and soivents (nitromethane, sulfoiane, THF and DMF) were studied. The reactions were carried out in sealed evacuated tubes in order to prevent any side reactions due to the presence of oxygen. The procedure used simply involved heating the polymer soiution with a large excess (greater than 10 times) of the aikyl haiide. The incorporation of the aikyl haiide into the poiymer was estimated from the weight gain

Table 2. Results of Quaternization of P2VP with CH_3Br (60°C, 24 hours in THF)

Sample[a]	MW (x10^{-3})[b]	Total Br (wt% Br)[c]	PyR^+ (mol%)[d]	Rad. Visc. (.10g/dL)[e]	ratio[f]
0521-L	5.24	-	70	222	.89
-C		-	73	199	
0630-L	14.60	-	66	.607	76
-C		-	69	.436	
0716-L	25.30	-	70	1.59	.55
-C		-	74	.872	
0707-L	25.00	34.7	72 (76)	1.45	.54
-C		33.4	73 (72)	.780	
0217-L	60.30	-	70	3.16	.95
-C		-	70	2.99	
0323-L	240.0	33.2	- (77)	18.0	83
-C		34.7	- (72)	15.0	

a. C = cyclic, L = linear
b. SEC molecular weight of linear precursor
c. total Br results from Atlantic Microlabs, Atlanta Ga.
d. % quaternization based on wt of product obtained (values in parenthesis are based on % Br analysis)
e. reduced viscosity in water (29.5°C) at c = .100 g/dL
f. ratio of reduced viscositias (cyclic/linear)

Table 3. Results of Quaternization of P2VP with Ethyl Bromide (18 hrs., 100°C in nitromethane)

Sample[a]	$\bar{M}_w$ ($\times 10^{-3}$)[b]	Total Br (wt%)[c]	PyH^+ (mol%)[d]	PyR^+ (mol%)[e]
0728-C	4.01	28.8	7	48
-L		26.9	8	47
0630-C	14.80	33.9	16	63
-L		33.7	20	57
0217-C	80.30	34.2	18	62
-L		33.0	19	58
0225-C	112.0	27.4	-	-
-L		27.3	-	-
911-L	~150	27.7	7	24

a. C = cyclic, L = linear
b. SEC molecular weight of linear precursor
c. % Br from Atlantic Microlabs, Atlanta Ga.
d. by titration with NaOH
e. mole % alkylated pyridine groups calculated by difference from % Br and % PyH^+ results

and elemental analysis of bromine. The ideal solvent for these reactions would be one in which the original polymer, the alkyl halide and the polyelectrolyte were all soluble. It was hoped that in the more polar solvents the reaction would remain homogeneous. In all the solvents used; however, precipitation occurred soon after the start of the reaction, but this did not seem to preclude high degrees of quaternization. Since the reaction seemed to go quite well even though it was heterogeneous, it was decided to try using THF as the solvent, as it has a much lower boiling point than the other solvents, and is thus much easier to remove from the reaction product. There was also the added advantage that a large amount of highly purified THF was readily avaible. The reactions carried out in THF resulted in products with degrees of quaternization comparable to those obtained in nitromethane and DMF. The reactions run in DMF gave yellow products, whereas in THF and nitromethane the reaction products were white. One reaction was done in CH_3Br without solvent. This reaction gave a respectable quaternization yield (~50 %) even though it was only done at room temperature. It is likely that at higher temperatures, this reaction would proceed to a higher degree. In all cases, the reactions yielded polymers which were completely soluble in H_2O and methanol, but insoluble in most other organic solvents. Methanol cannot be used as the quaternization solvent because of the

occurrence of alcoholysis of the alkyl halide, catalyzed by the pyridine groups of the polymer (45).

The first alkylating agent studied was CH_3I. This reaction gave a brown product, even when freshly distilled CH_3I was used. This brown color is presumably due to the presence of elemental iodine in the product. Even though this product is highly discolored, it is water soluble; and the degree of quaternization, based on the weight of the product obtained, appears to be very high (>50 %).

Experiments carried out using CH_3CH_2Br in nitromethane (see Table 3) at 40°C for 18 hours gave quaternized polymers which were shown by elemental analysis to contain approximately 30 % bromine by weight. These products did not show the discoloration that occured when CH_3I was used. The dilute solution viscosities of these polymers were studied in three different solvents and are discussed below. It was found that all the polymers reacted with CH_3CH_2Br gave acidic solutions in water. Several of these samples were titrated with standerdized NaOH in order to determine their acid content. Based on the % Br (by elemental analysis) and the acid content (by titration), it is possible to calculate the relative amounts of unreacted, alkylated, and protonated pyridine units in the samples. These results are included in Table 3. The high acidity of these samples is presumably due to elimination reactions catalyzed by the free pyridine groups in the polymer (see Figure 25). These reactions may involve either free ethyl

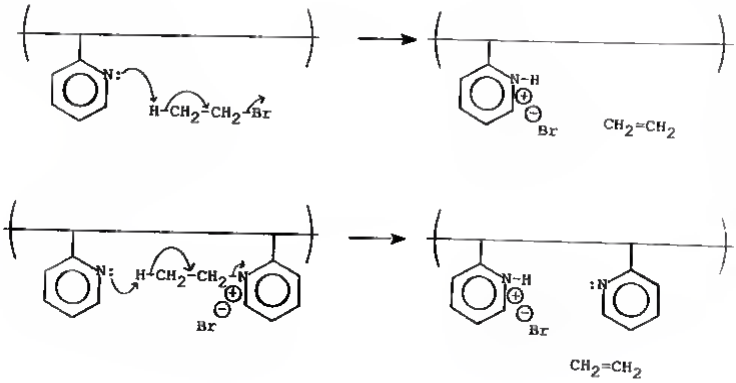


Figure 25. Elimination reactions in the P2VP/ethyl bromide system, leading to acidified polymer

bromide molecules or the N-ethyl groups of the quaternized polymer. It should be noted that for cyclic/linear pairs quaternized with CH_3CH_2Br under identical conditions, the ratio of alkylated to protonated pyridine units is, in all cases, higher for the cyclic polymers. There is no clear explanation for this unexpected result, although it could be due to conformational or solubility differences between the cyclic and linear polymers. In order to avoid these undesireable side reactions, CH_3Br was employed as the alkylating agent in subsequent runs. Beta-elimination reactions cannot occur with CH_3Br, and indeed, it was found that polymers quaternized with this reagent did not give acidic solutions when dissolved in water. The reaction of P2VP with CH_3Br in THF for 24 hours at 60°C consistently gave polymers in the form of white powders having approximately 70 mole% quaternization, which were also completely water soluble and not acidic (see Table 2).

Viscosities of Quaternized P2VP

Viscosities of the various quaternized polymers were determined in pure H_2O, methanol, and 1 M NaBr (aq). All of the quaternized polymers, regardless of conditions or alkylating agents, showed the expected sharp increases in reduced viscosity upon dilution in pure H_2O. In methanol, the reduced viscosities are somewhat lower, and the increase in reduced viscosity upon dilution is not as sharp. In 1 M NaBr (aq), plots of reduced viscosity vs. concentration are essentially linear, with a very slight increase in

the reduced viscosity upon dilution. The reduced viscosities are also lower than they are in methanol. Reduced viscosity vs. concentration plots in all three solvents for a sample of linear P2VP of molecular weight 60,000 quaternized with ethyl bromide are shown in Figure 26. The same trends are seen for all of the quaternized polymers. The sharp increase of the reduced viscosity in water upon dilution can be explained by a decrease in screening of the fixed positive charges by the counterions as described above. In methanol, due to the lower dielectric constant, the degree of dissociation of the ion pairs is much lower, and the positive charges are thus more effectively shielded from each other by the counterions. This results in less expansion of the polymer coil, and hence a lower reduced viscosity. In solutions containing a high salt concentration, the driving force for diffusion of the counterions out of the polymer domain is much less, so the shielding of the positive charges from each other is increased. This leads to less expansion of the chain, and even lower reduced viscosities.

Based on the results for the unquaternized polymers, the reduced viscosity at a given concentration is expected to be less for a cyclic polymer than for a linear polymer having the same chain length and degree of quaternization. Indeed, it is found in all cases, that for cyclic and linear polymers of the same chain length, quaternized under identical conditions, the reduced viscosities in methanol

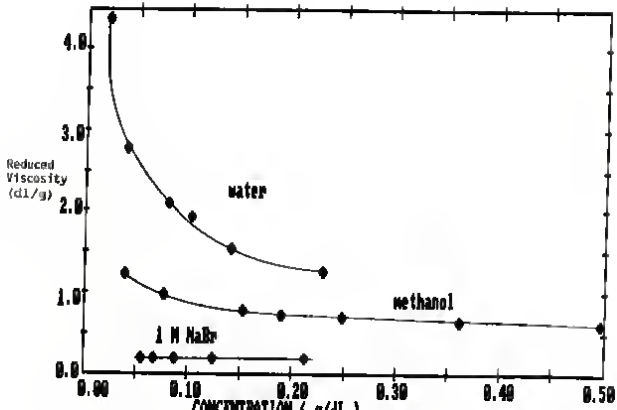


Figure 26. Plot of reduced viscosity (T=29.5°C) vs. concentration in three different solvents, for a linear P2VP sample of molecular weight 60,000 quaternized with ethyl bromide

or in salt solution are lower for the cyclic polymers (see Figure 27). The same result is found in H_2O for poylmers quaternized with CH_3Br. Cyclic and linear polymers of the same molecular weight quaternized with CH_3CH_2Br; however, exhibit practically identical reduced viscosities in H_2O in all cases (see Figure 28), even though the reduced viscosities of the same pairs of polymers in methanol or in salt solution are different. This discrepancy is most likely due to the presence of the acidified pyridine groups in the polymers quaternized with ethyl bromide. It was noted above that the cyclic polymers were found in all cases to contain a higher percentage of alkylated pyridine units (PyR^+), and a lower percentage of protonated pyridine units (PyH^+), than the linear polymers quaternized under the same conditions. In water, the protonated and alkylated pyridinium groups are expected to behave quite differently. For the alkylated polyvinylpyridinium ions, only dissociation of the PyR^+,X^- ion pair may occur:

$$PyR^+,X^- \rightleftharpoons PyR^+ + X^-$$

The PyH^+ ions; however, may donate a proton to water, resulting in neutral pyridine groups:

$$PyH^+,X^- \xrightleftharpoons{H_2O} Py + H_3O^+ + X^-$$

The extent of both reactions is expected to increase upon dilution. At a polymer concentration of .100 g/dl, the concentration of PyH^+ groups in these samples is on the

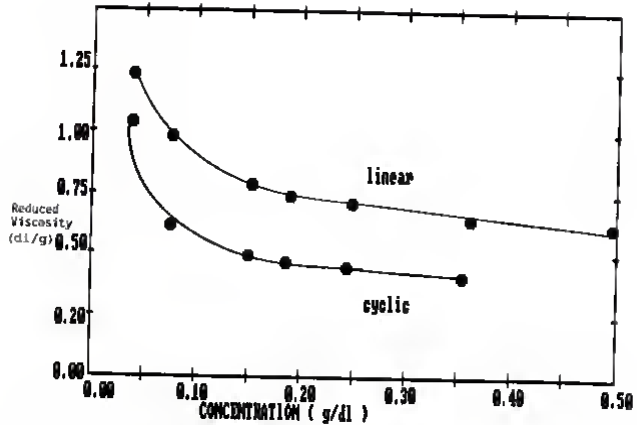


Figure 27. Plot of reduced viscosity (T=29.5°C, methanol) vs. concentration for cyclic and linear P2VP (MW ~ 60,000), quaternized with ethyl bromide under identical conditions

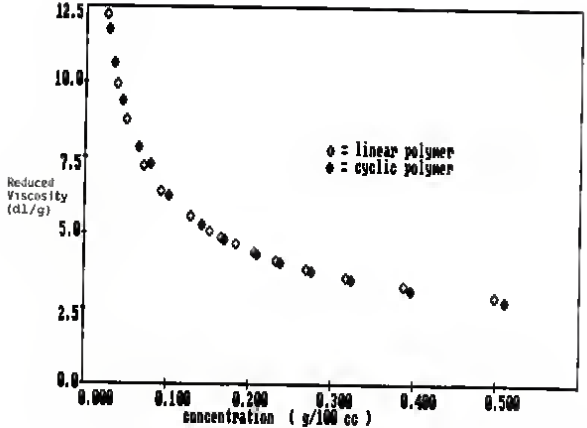


Figure 28 Plot of reduced viscosity (T=29.5°C, water) vs concentration for cyclic and linear P2VP (MW = 112,000) quaternized with ethyl bromide under identical conditions

order of 10^{-5}M. Calculations show that a 10^{-5}M solution of monomeric hydrogen pyridinium bromide will be approximately 30% deprotonated in water. This calculation does not take into account the fact that the pyridinium groups are contained in a polymer which also contains a large number of alkylated pyridinium groups (which do not dissociate, but do carry a positive charge). It follows that due to electrostatic effects from the PyR^+ groups, the driving force for the deprotonation of the PyH^+ groups should be increased, and at these low concentrations the deprotonation should be almost complete. The polymers containing both PyH^+ and PyR^+ groups thus loose some of their polyelectrolyte character upon dilution in water and this results in a lower reduced viscosity. Since the linear samples quaternized with CH_3CH_2Br are more highly protonated than the corresponding cyclic polyelectrolytes, this loss of reduced viscosity is more pronounced. This effect is expected to be counteracted; however, by the inherently larger dimensions of the linear polymer. Apparently, in the case of the polymers shown in Figure 28, the two effects seem to exactly balance. This interpretation is consistent with the fact that in methanol or 1M NaBr (where polyion expansion is repressed), the reduced viscosities of the cyclic polyelectrolytes are substantially less than those of the linear polyelectrolytes. This is roughly similar to the situation in the case of the uncharged polymers. Further evidence is provided by the

fact that the reduced viscosities in all solvents, including water, are consistently less for cyclic than for linear P2VP quaternized with CH_3Br. In this case, the polymers are only alkylated (not protonated), consistent with the absence of elimination reactions occuring during alkylation. In order to more fully understand this rather complex system, it would be necessary to conduct further experiments; but since the goal of this work is to produce well-defined macrocyclic polyelectrolytes, further studies of this rather complicated and ill-defined syetem are not warranted. Instead, it was decided to concentrate on the use of CH_3Br as an alkylating agent since this does not involve these complications.

For the polymers quaternized with CH_3Br, it was found that in all cases, and in all solvents, the quaternized cyclic polymers had lower reduced viscosities than did their corresponding linear counterparts. Since it is not possible to determine intrinsic viscosities of these polymers in water, due to the curved nature of the reduced viscosity vs. concentration plots, values of the reduced viscosity at C = .100 g/dl were used in order to compare the various samples. These values for the cyclic and linear polymers quaternized with CH_3Br in THF are shown in Table 2. Several things are readily apparent. First, in all cases, the cyclic polymers have lower reduced viscosities than do their linear precursors. Second, the viscosities increase with increasing molecular weight, as

expected. There is some variation in the ratios of the viscosities of the cyclic/linear pairs, but this is most likely due to variations in the degree of quaternization of the samples. This is to be expected, since the quaternization reaction is heterogeneous in nature. In order to fully understand the effect which the degree of quaternization has on the viscosity of the polymer solutions, it will be necessary to conduct careful studies involving polymers having different degrees of quaternization. For polymers having different degrees of quaternization, the differences in the reduced viscosities due to electrostatic effects can be minimized by doing the measurements in salt solution rather than in water. It would also be informative to compare the reduced viscosities at a given concentration of polymer chains, rather than at a given weight concentration, because a polymer with a higher degree of quaternization has a higher actual molecular weight. At a given weight concentration, a more highly quaternized sample of a given chain length may actually exhibit a lower reduced viscosity than a sample with the same chain length, but having a lower degree of quaternization. This is because, although the more highly quaternized chains are more expended, there is a lower number of these chains in the solution. Such studies should serve to clarify the behavior of this rather complicated system. It is clear, however, that macrocyclic polyelectrolytes have indeed been prepared.

CHAPTER 5

THREE-ARM STAR P2VP BY COUPLING

A series of three-arm star P2VP's was prepared by coupling three living P2VP chains using 1,3,5-tris(chloromethyl)benzene (TCMB). The procedure that was used is described in Chapter 2. The monofunctional living linear precursor was prepared at -78°C in THF using 2-ethylpyridyllithium (2EPLi) as initiator. This initiator was shown to produce monodisperse P2VP (see below). The coupling reaction was carried out in the same flask that was used to prepare the living precursor. This avoided any unnecessary manipulation of the living polymer solutions which might lead to partial deactivation of the living ends. Similar reaction schemes have been used by others to prepare star-branched polystyrene (23,47), but in the present work the use of a glass frit allows for better control of the rate of addition of the coupling agent, and thus may lead to products with a higher degree of structural integrity. After the precursor was prepared, a portion of it was isolated in a side arm and protonated with degassed methanol. This allowed a determination of the molecular weight of the individual branches in the star polymer. This linear precursor was also essential in evaluating the success of the coupling reaction, because it

allowed a comparison of the SEC traces of the linear precursor and the coupled product.

The basic strategy used for the coupling reaction was to rapidly add approximately 80 to 90% of the required amount of coupling agent to the living polymer solution, and after reaction, to add the remainder of the TCMB dropwise, thus ensuring the addition of a stoichiometric amount of the coupling agent. The progress of the reaction was monitored visually by observing the disappearence of the red color of the living P2VP chain ends. It was observed that the red color diminished in intensity immediately upon addition of coupling agent. This is expected, since the reaction of a P2VP carbanion with a benzylic chloromethyl group is very fast (see discussion of cyclization reaction in Chapter 3). A further decrease in the intensity of the red color was observed within one to two minutes after the initial addition of coupling agent. This is consistent with the expectation that the rate of addition of the third arm should be less than the rate of the first or second, due to effects of excluded volume, because the third coupling step involves approach of a living chain-end to a chloromethyl group which is at the center of an existing polymer chain (47). Likewise, the rate of the second substitution reaction should be less than that of the first, but in this case there are two possible reaction sites, and they are located on an end, rather then in the center of the chain. No similar time lag was observed in

the cyclization reaction of living P2VP, where only reactions involving chain ends occur. The observation of a graduai fading of the red color indicates that the difference between the rates of addition of the first and second arms is much iess than the difference between rates of addition of the second and third arms. A similar observation has been reported by Roovers, in the reaction of living polystyrene with 1,2-bis(methyldichiorosilyl)ethane (48).

The method used for the coupling reaction does not lend itself to the formation of "two-arm" star in any appreciable quantities. This is because the coupling agent used was quantitatively trifunctional (more than 99.8%), and it was added very slowly towards the end of the coupling reaction, thus ensuring that complete substitution occured. There is however, the possibility that "one-armed" star is produced by accidental deactivation of the parent living polymer. As will be seen in the discussion of the SEC results presented below, at least some of these dead arms were present in the product mixtures in all cases. These do not pose a significant problem, because as demonstrated in the fractionation of macrocyclic P2VP, the quantitative separation of high and low molecular weight P2VP can be accomplished quite easily by solvent fractionation. Such a purification was not attempted; however, in the case of the star polymers. Furthermore, the fraction of deactivated linear precursor is low, and in such a case

Table 4 SEC Data for Three-arm Star P2VP

Sample	M(arm)[a]	(Mw/Mn)	M(star)[b]	<G>[c]	<g'>[d]
1	8,700	(1.04)	25,300	.97	.95
2	21,100	(1.02)	62,400	.98	.97
3	21,600	(1.02)	63,100	.97	.95
4	92,000	(1.02)	267,000	.96	.93
5	94,000	(1.06)	275,000	.97	.95
6	163,000	(1.05)	463,000	.95	.92

a. SEC molecular weight of linear precursor, based on calibration with linear standards

b. SEC molecular weight of coupled product, based on calibration with linear standards

c. ratio of M(star)/3 to M(arm)

d. ratio of intrinsic viscosities of star and linear P2VP of equal molecular weight, calculated from Equation III (chapter 3) using a = .56

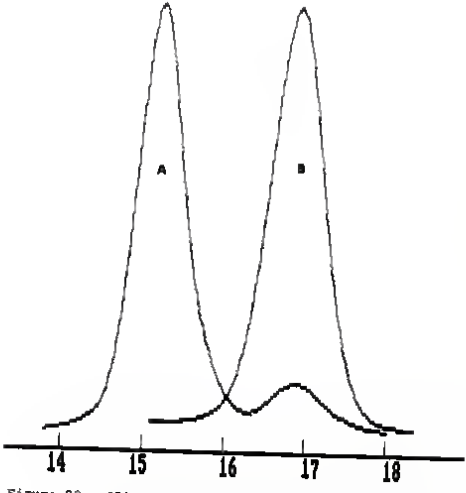


Figure 29. SEC traces of the product of the coupling reaction between living P2VP and TCMB (A), and the living linear P2VP precursor (B)

the SEC peak maximum reflects the molecular weight of the star polymer and is not influenced by the impurity.

A series of three-arm star P2VP's was prepared using the method described above. The molecular weights of the precursors used in these reactions ranged from approximately 10,000 to 160,000. The precursors and the products of the coupling reaction were analyzed by SEC using the same methods as described for the analysis of macrocyclic P2VP. The SEC results are summarized in Table 4. A comparison of the SEC traces of the precursor and the coupled product for entry #1 (Table 4) is shown in Figure 29. It can be seen that a small fraction of terminated chains (precursors) are present in the reaction product. Such terminated chains were found in all the reaction products, but by carefully controlling the procedures used, the amount of these linear impurities can be kept to less than a few percent. As expected, the coupled products have elution volumes lower than those of the precursors, and SEC molecular weights which are approximately three times higher than those of the precursors. The absence of any two-arm polymer is indicated by the fact that the widths of the SEC peaks of the coupled products are very narrow and comparable to those of the precursors from which they were obtained. In several runs, the coupled products showed SEC peaks which were much broader than those of the precursors. In such cases the ratio of the SEC molecular weights of the products to the precursors was generally closer to 2 than

to 3. This is good evidence that the broad peaks obtained in these cases were due to significant amounts of two-armed polymer. Such polymer was presumably formed by an inadvertent addition of excess coupling agent. The results of such runs have been discarded. In some cases, the widths of the peaks from the coupled products are actually narrower than the peaks from the precursors (see Figure 29). Such an effect is understandable by considering that variations in chain length can be averaged out by the coupling of three chains (4). The same effect has been reported in the case of eighteen-arm star polybutadiene (43). The direct comparison of the SEC molecular weights of the coupled product and the linear precursors is not a good comparison since the two polymers contain different numbers of repeat units. It is of much more value to compare the ratios of the SEC molecular weights of polymers having the same number of units. In order to make such a comparison, the SEC molecular weights of the linear precursors have been multiplied by a factor of three (see Table 4). The resulting ratio of the SEC molecular weights of star and linear polymers having the same number of units is denoted by <G>. Note that this term has the same meaning as it did in the discussion of cyclic polymers in Chapter 3. It is evident that this value is slightly less than 1.00 in all cases, but not by very much. It should be pointed out that while these values are all very close to

1.00, they are all consistently lower, and thus it seems that the observed deviation from unity is, in fact, real.

The analysis of dimensions of star polymers in solution is quite similar to the analysis of the dimensions of macrocyclic polymers. In both cases, geometric constraints result in polymers which have higher segment densities and smaller overall dimensions than linear chains with the same number of units. Thus, it is possible to use the same terminology and relationships to discuss the dimensions of star polymers in solution as were used to discuss the dimensions of cyclic polymers in Chapter 3. The terms <G> and <g'> were used to represent, respectively, the ratios of SEC peak molecular weights and of intrinsic viscosities, for cyclic and linear polymers having the same number of units. These same symbols can be used when discussing the corresponding ratios for three-arm star polymers. The relationship between <G> and <g'> has been derived by Jordan and McConnell (34). This relationship ($<G> = <g'>^{1/1+a}$) was given in Chapter 3 (Equation III). Under theta conditions (a = 0.5) this reduces to ($<G> = <g'>^{2/3}$). In order to facilitate comparison of the SEC data for three-arm star P2VP with theoretical predictions and the experimental results for other polymers, the values of <G> in Table 4 were converted to the corresponding <g'> values (using a = 0.66, see Chapter 3). The values calculated in this manner range from 0.92 to 0.97 (see Table 4).

There have been numerous theoretical predictions concerning the relative solution dimensions of star and linear polymers having the same number of units (49-51). Many of these theories are based on rather simple models, and thus may not adequately describe real systems. A value for <g'> of 0.88 for all three-arm star polymers is predicted on the basis of the calculations of Zimm and Stockmayer (50). These calculations are based on a simple random-walk model, and thus do not account for any excluded volume effects. Monte-Carlo simulations of random-walk star-branched polymer chains with excluded volume (long-range interaction between chain segments) predict <g'> values of up to approximately 0.92 (51). The theoretical treatment of Zimm and Kilb (52) is based on a random-walk model which takes interaction between chain segments into account, and predicts a value of <g'> equal to approximately 0.91.

There are no reports in the literature of the synthesis of three-arm star polymers of P2VP, but there are several reports of the preparation of three-arm star polystyrene. There is however, a suprising lack of clear SEC analyses of these systems. Bryce et al. (23) reported SEC analyses of three-arm star polystyrenes, but did not fully evaluate these results with respect to the relative dimensions of the branched and linear chains in solution. Several reports of the experimental determination of the ratios of intrinsic viscosities of three-arm star and linear polystyrenes of the same molecular weight have been

published (47,53). There is a large amount of scatter in the values of <g'> reported by these various groups. The reported values range from 0.81 to 0.95, and there are conflicting reports as to whether this ratio increases or decreases upon going from a theta solvent to a good solvent. It is clear however, that the bulk of these values are close to the values predicted by the various theoretical models.

The values of <g'> for the three-arm star P2VP are in reasonable agreement with the results for polystyrene, but it appears that these ratios are a little higher than predicted theoretically. This result supports the claim that the polymers produced are indeed true three-arm star polymers and are not contaminated by any significant amount of "two-arm star". It may be argued that the presence of some four-arm star in the samples (formed either by side reactions - see chapter 7; or by the presence of some tetrafunctional coupling agent) would also make the ratios <g'> and <G> higher than predicted for a three-arm star, but this possibility can be ruled out based upon the narrow molecular weight distributions observed for the coupled products, and the purity of the coupling agent which was used.

The star-branching constraint limits the volume in which the macromolecule would be contained if it were fully extended; however, the average dimensions of the chain in solution are much less than this value (just as they are in

the case of a linear polymer). The average dimensions of a star polymer in solution may be perturbed by the higher segment density and an increase in excluded volume effects near the center of the coil (caused by the close linkage of three chains). This would be expected to result in a net expansion of the star polymer. Such an effect would explain why the values of <G> observed in both the polystyrene and P2VP cases are higher than predicted by the simple random-walk model.

The apparent deviation from the theoretically predicted ratios of the sizes of star and linear polymers may also be caused by the presence of the rather rigid coupling agent moiety. This may serve to keep the three chains separated to a significantly higher degree than if the size of the coupling agent were negligible compared to the dimensions of the polymer coils. The use of TCMB as the coupling agent keeps the three polymer chains separated from each other by approximately 6 angstroms. This is a considerable distance, considering that the average radius of a P2VP coil of molecular weight 10,000 in solution is approximately 30 angstroms.

Based on the SEC results, the cyclization constraint appears to exert a much greater effect on the dimensions of the macromolecule than does the constraint of restricting it to the geometry of a three-arm star. The lack of a pronounced systematic variation in the values of <G> with molecular weight is not too suprising, since the magnitude

of the decrease in hydrodynamic volume is rather small to begin with, and any variation may be obscured by the uncertainty in the measurement of what is already a very small effect. For star polymers having more than three arms, lower values of <G>, and a pronounced dependance of <G> on molecular weight (similar to what is observed in the case of macrocyclic P2VP), are expected. As pointed out previously, such an effect has been seen in the case of highly branched comb-type polystyrene (39).

It should be mentioned that attempts were also made to prepare three-arm star polymers using CH_3SiCl_3 as the coupling agent. Experiments carried out using this coupling agent did not give well-defined products. It appeared that in this case the coupling was incomplete and that the products contained a large amount of terminated precursor. Such results are presumably due to steric effects which hinder the addition of the third arm, side reactions (studies of model compounds revealed the occurence of reactions other than the expected nucleophilic substitution), and/or to difficulty in adequately purifying small quantities of CH_3SiCl_3 necessary for the reaction. It should be pointed out that TCMB is a relatively stable crystalline solid and is thus much easier to work with than is CH_3SiCl_3.

It has been demonstrated that well-defined three-arm star polymers of 2VP can be prepared in good yield by coupling three living P2VP chains with a trifunctional

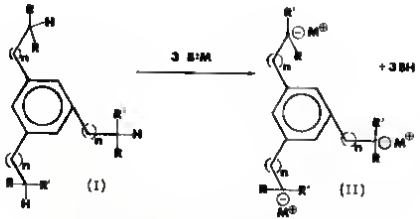
coupling agent (TCMB). Such polymers in THF solution have a hydrodynamic volume which is slightly less than that of linear P2VP having the same number of units. This value is consistent with the results for three-arm star polystyrene and is slightly higher than what is predicted on the basis of theoretical models.

CHAPTER 6

PREPARATION OF TRIFUNCTIONAL CARBANION INITIATORS

Attempts were made to prepare trifunctional initiators via the reaction scheme shown in Figure 30. In each case, the anions are "insulated" from each other, and from the center ring, by a methylene spacer group which prevents interactions between the anions through resonance. Identification of trifunctional anions made in this manner can be accomplished by quenching the reaction mixtures with methyl iodide followed by GC analysis of the methylated products. The mono-, di- and trifunctional carbanions should give the corresponding mono-, di- and trimethylated compounds, which are expected to have different GC retention times. In order to obtain a useful trifunctional initiator, it is necessary that the deprotonation be quantitative when a stoichiometric amount of base is used (see chapter 1), however, in peliminery deprotonation attempts, an excess of base was used in order to determine whether the deprotonation was in fact possible.

An attempt to deprotonate compound (Ia), using n-butyllithium in THF was unsucessful (no red color, characteristic of the diphenylalkyl carbanion was apparent). Subsequent ettempts at this reaction, using sec-butyllithium, tert-butyllithium and a n-butyllithium/



I_a, II_a: R=R'-phenyl, n=1
I_b, II_b: R=H, R'=2-pyridine, n=1
I_c, II_c: R=methyl, R'=2-pyridine, n=1
I_d, II_d: R=R'-phenyl, n=2
I_e, II_e: R=H, R'=2-pyridine, n=2

Figure 30: Reaction scheme for the preparation of trifunctional carbanion initiators

tetramethylpropanediamine complex in hexane also proved unsuccessful. This reaction did not occur even when the temperature was raised from -78°C to 0°C. This result is unexpected, because the corresponding reaction with 1,1-diphenyl ethane is known to occur rapidly (54). It was anticipated that steric effects due to the other two substituents on the center ring were responsible for this lack of reactivity; however, when an attempt was made to see if the corresponding 1,1,2-triphenylethane would undergo reaction under the same conditions, the results were exactly like those mentioned above. It is clear; therefore, that it is the center ring which somehow prevents the deprotonation of (Ia).

The deprotonation of (Ib) met with considerably more success. The reaction of (Ib) with n-butyllithium in THF was rapid and resulted in a solution with the deep red color characteristic of alkylpyridyl carbanions. Upon quenching this solution with CH_3I followed by GC analysis, it was evident that reactions other than those illustrated in Figure 30 were occuring. Identification of the methylation products of anion (IIb) was facilitated, owing to the stereochemistry of the various methylation products. Compound (Ic) contains three topologically equivalent chiral centers, and hence exists in two diastereomeric forms, (RRR) and (RRS, RSR and SRR). Statistically, these should be formed in the ratio of 1:3. The dimethyl product (which results if only two of the three protons are

removed), on the other hand, has only two chiral centers and thus should exist in two diastereomeric forms in the ratio of 1:1. These different diastereomers are readily seperated by capillary GC. The monomethylated product and the starting material both exist in only one form and thus each show only one GC peak. Capillary GC analysis of the methylated products from the reaction of (Ib) with butyllithium reveals several groups of peaks (see Figure 31). Each of these groups of peaks appears to contain pairs of peaks in the ratio of 1:3 and 1:1. It was assumed that the group of peaks with the lowest retention time corresponded to the products from the simple deprotonation reactions described above, since the retention times for this group were very close to that of the starting material. Since nucleophilic attack on pyridine rings is well known (55), it seems likely that the different groups of peaks may correspond to different extents of the addition of butyllithium to the three pyridine rings in the precursor. This is accompanied by the expected deprotonation reactions, hence the apparent stereochemistry of each group. In any event, there are some side reactions occuring and this makes the system unsuitable for the preparation of a well defined trifunctional carbanion.

The reaction of (Ib) with a stoichiometric amount of 1,4-dilithio-1,1,4,4-tetraphenylbutane (DD^{-2}) resulted in the expected deprotonation products with no evidence for the occurence of any side reactions. This reaction is not

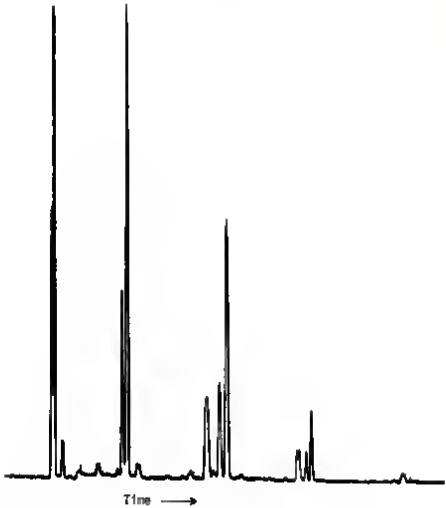


Figure 3i. Capillary GC analysis of the products of the reaction of TEP9 with excess n-BuLi in THF, after quenching with CH_3I

useful; however, because an excess of the base is needed in order to obtain quantitative deprotonation. The methylation products from this reaction clearly show the expected ratios for the various diastereomers (see Figure 32). It is interesting to note that the mono-, di- and trimethylated products appear at retention times which are increasingly lower than that of the starting compound (Ib). The absence of side reactions is consistent with the lower nucleophilicity of DD^{-2} compared to butyllithium, but it is obvious that a stronger base must be used in order to have stoichiometric deprotonation.

The reaction of (Ib) with dipotassio-alphamethylstyrene dimer resulted in a clean reaction with straightforward stereochemistry. This reaction proceeded cleanly and rapidly, yielding tris-anion (IIb) quantitatively, as demonstrated by formation of trimethyl product (Ic) upon quenching with methyl iodide (see Figure 33). In order to ascertain whether this product was actually compound (Ic), this compound was synthesized by an independent route (addition of 2EPLi to TCMB). The compound prepared in this manner gave GC peaks identical to those in Figure 31. Confirmation of this structure and additional proof that the two compounds were one and the same was made by proton NMR (see Figure 34). It is clear, therefore, that anion (IIb) is produced quantitatively with only trace amounts of the dienion or other carbanion by-products.

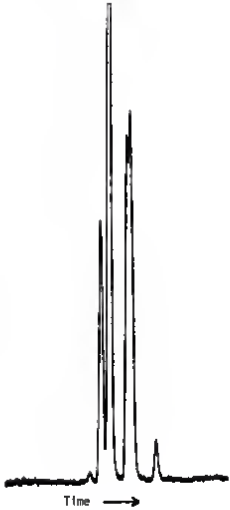


Figure 32. Capillary GC analysis of the products of the reaction of TEPB with excess 1,1-dilithio-1,1,4,4-tetraphenylbutane in THF, after quenching with methyl iodide

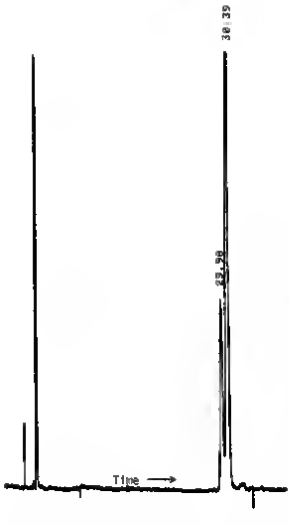


Figure 33. Capillary GC analysis of the products of the reaction of TEPB with a stoichiometric amount of dipotassio-alphamethylstyrene oligomers, after quenching with methyl iodide

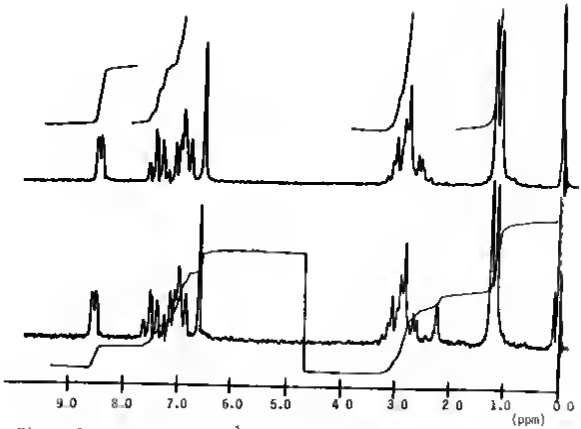


Figure 34. Comparison of ^{1}H-NMR spectra of 1,3,5-tris[2-(2'-pyridyl)propyl]benzene prepared by quenching of tris-anion of TEPB with methyl iodide (top), and by reaction of methylpyridyllithium with TCMB (bottom)

This anion (IIb) was used therefore, as initiator in the polymerization of 2-VP and 4-VP. In each case, a broad molecular weight distribution polymer resulted. In all cases, it was found that a significant proportion of the initiator remained unreacted. The reasons for these results were unclear. Hence, it was decided to study the oligomerization of this system. Between three and five mole equivalents of either 2-VP or 4-VP were added to one equivalent of tris-anion (IIb). These experiments were done at various temperatures ranging from -78°C to 25°C, and for varying lengths of time. A significant amount of initiator was always found to remain after the addition of monomer (in some cases, as much as 90% of the initiator had not reacted). These results indicate that the trifunctional carbanion which has been prepared is, for some unknown reason, inherently unreactive. This low reactivity towards monomer explains why broad molecular weight distribution polymers are produced.

The surprising lack of reactivity of (Ia) towards butyllithium in THF is clarified by the similar lack of reactivity of 1,1,2-triphenylethane. Apparently this lack of reactivity is not due to mutual steric interactions between the three substituents on the central ring of (Ia). Inspection of CPK space-filling models indeed reveals that the formation of the 1-lithio-1,1,2-triphenylethane is hindered by non-bonded interactions between the 2-phenyl and the 1-phenyl groups, and that the anion should form

less easily than those of diphenylethane or triphenylethane, for instance. This lessened reactivity due to the presence of a phenyl group in the 2- position, may also be responsible for the occurence of side reactions in the reaction of (Ib) with butyllithium. Even though it is known that butyllithium can add to pyridine rings, such reactions are not observed when butyllithium is reacted with 2-ethylpryidine. In the later case, only deprotonation is observed (56). This also suggests that such effects involving the center ring might be responsible for the lack of reactivity of anion (IIb) towards monomer. A space-filling model of (IIb) did not reveal any severe non-bonded interactions which would seem to hinder the addition of monomer; furthermore, on the basis of these models, it is unlikely that mutual steric interactions between the three substituents causes the lack of reactivity. This leaves some type of interaction with the center ring as the most probable explanation for the observed behavior. The lack of reactivity of the 1-lithio-1-(2-pyridyl)-2-phenylethyl grouping present in (IIb) is of particular interest because it is known that 1-lithio-1-(2-pyridyl)-3-phenylpropane (Figure 35a) is a good initiator for 2-VP (56). Examination of CPK models of the 1:1 adducts of these anions with 2-VP, suggests that non-bonded interactions are present in the former (Figure 35d), but not in the latter case (Figure 35c). For instance, in models of the molecule pictured in Figure 35d, there are unfavorable steric

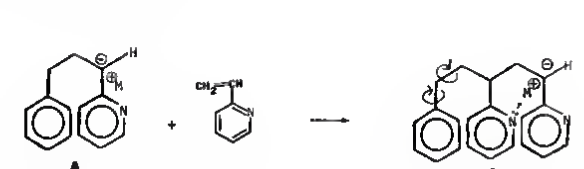


Figure 35 (A) 1-lithio-1-(2'-pyridyl)-3-phenylpropane
(B) 1-lithio-1-(2'-pyridyl)-2-phenylethane
(C) Addition product of (A) with 2VP monomer
(D) Addition product of (B) with 2VP monomer

interactions between the center ring and the pyridine rings. On the other hand, the model of the compound in Figure 35c reveals no such unfavorable interactions. These non-bonded interactions may serve to interupt the coordination of the counterion with the penultimate pyridine nitrogen. Such coordination is known to have a stabilizing effect in the living P2VP system (57). It is evident therefore, that addition of monomer to anion (IIb) is expected to be a slow reaction because it results in the formation of a higher energy intermediate (Figure 35d). Subsequent addition steps should proceed in a normal fashion, uncomplicated by affects from the center ring. The net result is that the initiation step is slow compared to propagation, and this explains both the broad molecular weight distribution and the finding of unreacted initiator in the reaction mixture, even when the more reactive 4-VP is used.

It was desired to investigate the effect of having a longer spacer unit between the active sites and the center ring. Compound (Id) was synthesized and its deprotonation was studied; however, a satisfactory synthesis of the analogous alkylpyridine derivative (Ie) could not be devised. It was found that (Id) did not react with n-, sec-, or tert-butyllithium at -78°C in THF. At higher temperatures, some deprotonation occured, but at these temperatures there is a competing reaction of butyllithium with THF (4)

Attempts were made to deprotonate (Id) with potassio-alphamethylstyrene dimer. This resulted in partial deprotonation, but only if high temperatures, a large excess of the deprotonating agent and, long reaction times were used. It was decided that this system did not look promising and no further studies were carried out.

Although a well-defined tris-anion (IIb) was prepared, it was found to be a poor initiator for 2VP. It is very possible; however, that it may be a useful initiator for a more reactive monomer such as methyl methacrylate or cyclotri(dimethylsiloxane). Such experiments were not attempted.

CHAPTER 7

SIDE REACTIONS IN LIVING P2VP SOLUTIONS

During the course of the work on the synthesis of macrocyclic P2VP, it was discovered that if solutions of living P2VP in THF are allowed to stand at room temperature, a high molecular weight shoulder develops in the SEC chromatograms of such polymers. This shoulder appears as a distinct peak with a molecular weight double that of the main peak. In no case does this small peak ever account for more than approximately 10% of the total polymer in the sample. It was determined that such peaks formed only when the solutions were allowed to stand at room temperature for periods longer than about 15 minutes. These changes were accompanied by a darkening of the solution from the bright cherry-red color, characteristic of the living P2VP anions, to a more brownish-red color.

In order to clarify the nature of the reactions responsible for the observed changes, a solution of two-ended living P2VP was prepared using DD^{-2} as initiator (as described in the experimental section; carbanion concentration ~5 x 10^{-3}M), and divided into four separate portions. These solutions were stored at various temperatures, for various lengths of time, as specified in Figure 36. After aging, the solutions were terminated with thoroughly

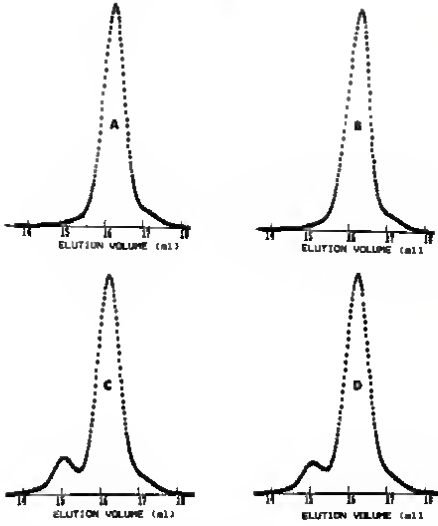


Figure 36. SEC traces of living (difunctional) P2VP solutions quenched with methanol after storage under the conditions indicated:

(A) 0°C - 5 minutes (B) -78°C - 17 hours
(C) 25°C - 2 hours (D) 25°C - 17 hours

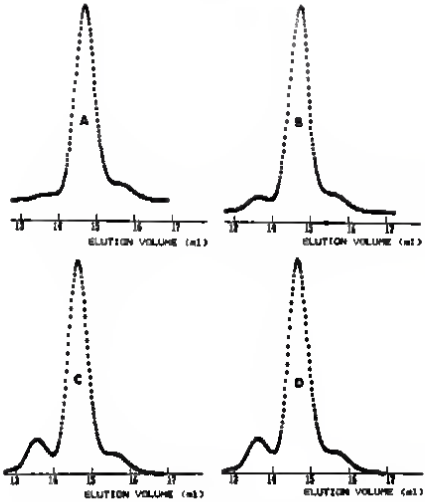


Figure 37. SEC traces of living (difunctional) P2VP solutions quenched with methanol/HCl after storage under the conditions indicated:

(A) 0°C - 2 hours (B) 25°C - 0.5 hours
(C) 25°C - 2 hours (D) 25°C - 2 hours

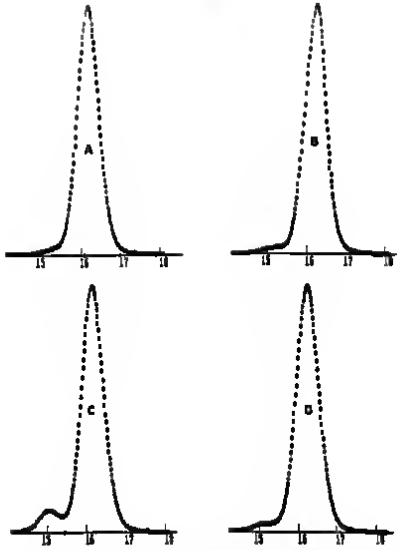


Figure 38. SEC traces of living (monofunctional) P2VP solutions quenched with methanol after storage under the conditions indicated:

(A) -78°C - 70 hours (B) 25°C - 0.5 hours
(C) 25°C - 2 hours (D) 25°C - 70 hours

degassed methanol. In freshly prepared solutions, and solutions which had been kept at -78°C, the red color of the living P2VP dissappeared immediately upon addition of methanol, and the solutions became colorless. Solutions which had been allowed to age at room temperature, however, remained yellow after the red color had disappeared. This yellow color faded after a few minutes and the solutions were then colorless. The SEC chromatograms of the resulting polymers are shown in Figure 36. This experiment was repeated using slightly different storage times and temperatures, as indicated in Figure 37. In this experiment, the solutions were terminated with a mixture of methanol and HCl (for reasons discussed below). The experiment was repeated one more time using monofunctional initiator. The times, temperatures and results of this experiment are summarized in Figure 38. It can be seen that the results in Figure 37 are very similar to those in Figure 36. The peaks in Figure 37 all have a low molecular weight shoulder. This is due to some premature termination of the initiator, and does not have any adverse effects on the results of this experiment. The polymer in Figure 37 has a molecular weight three times that in Figure 36, but the extent of the side reaction is identical in both cases. The polymer in Figure 38 has a molecular weight equal to that of the polymer in Figure 36, but has only one living end. The amount of high molecular weight species formed in this case is almost exactly half that in Figures 36 or 37.

Solutions stored at -78°C for up to 70 hours, or at higher temperatures for very short times, show no evidence for the formation of a high molecular weight species (Figures 36a, 36b, and 38a). Solutions stored at 0°C for two hours show a very small amount of high molecular weight product (Figure 37a). When the solutions are stored at 25°C, a significant shoulder appears after 30 minutes (Figures 37b and 38b). The high molecular weight peak seems to reach maximum intensity after two hours at 25°C (Figures 36c, 37c, and 38c). The size of this peak decreases slightly after seventeen hours at 25°C (Figure 36d), and even more so after seventy hours (Figure 38d). After two hours at 50°C, the size of the peak is identical to that in the solutions stored at 25°C for the same length of time (Figure 37d).

A solution of two-ended living P2VP in THF was prepared in an apparatus equipped with a UV cell. The UV spectrum of this solution was monitored as a function of time at room temperature. The intensity of the peak due to the living P2VP carbanion (315 nm) was seen to exponentially decrease from .80 AU to .69 AU during the course of about 48 hours. No further decrease in the intensity of this peak was observed, even after two months storage at room temperature. This corresponds to destruction of approximately 14 % of the original living P2VP chain ends, assuming that no new species are formed which absorb at 315 nm. There were other small changes in the UV spectrum of

aged living P2VP solutions noted in the region between 425 and 525 nm. It appears that one or more broad peaks are developing in this region. The magnitude of these peaks is however, very small.

In order to try and get some idea of the chain end structures involved in these side reactions, a low molecular weight living P2VP sample was prepared (DP ~10). This solution was divided into two portions. One portion was stored at -78°C for two hours and the other was stored at 25°C for two hours. Both solutions were then terminated with carbon-13 labeled methyl iodide. Carbon-13 NMR revealed that the sample stored at 25°C had at least two peaks (23.0 and 24.0 ppm) present in the methyl region of the spectrum which were not present in the sample which had been kept cold (see Figure 39). This indicates that end-group structures other than the "normal" methylation product (58) are present in the sample which was not kept cold.

It is clear that the new peak which appears in the SEC chromatograms of living P2VP solutions stored at room temperature is due to the coupling of two chains to produce a species having a molecular weight double that of the original polymer. A possible first explanation for this is nucleophilic attack by the living chain end on the pyridine rings in the polymer. Such reactions have been proposed to occur in living P2VP systems (59,60), but very little conclusive evidence for their occurence is presented. Such

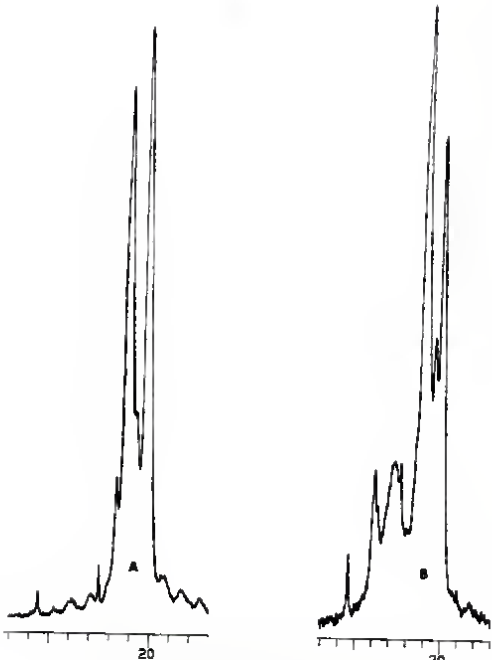


Figure 39. ^{13}C-NMR spectra (methyl region) of P2VP terminated with labeled methyl iodide
left - stored at -78°C for 2 hours before termination
right - stored at 25°C for 2 hours before termination

reactions would be expected to result in a broadening of the molecular weight distribution of the original SEC peak, as well as the formation of higher molecular weight material also having a broad distribution, due to "back-biting" (intramolecular) and "cross-linking" reactions which are expected to occur if random attack on the pyridine rings of the polymer chain were happening. Such a mechanism can be ruled out, because the new peak is seen to be relatively sharp and well-defined, and the distribution of the original peak remains unchanged. For this reason, it seems likely that a direct coupling involving two chain ends is involved. As pointed out previously, the amount of high molecular weight product formed when monofunctional initiator is used, is one-half that which is formed when the chains are difunctional. This is consistent with a direct coupling of two chain ends.

An alternative explanation involves the coupling of chain ends, due to reactions involving electron transfer to oxygen. Coupling reactions of living polymer chains caused by the presence of oxygen (and CO_2) are well known (61), but can be ruled out in this case, because oxygen was rigorously excluded from the system. An SEC chromatogram of a living P2VP solution which was intentionaly terminated by exposure to air is shown in Figure 40. It can be seen that the extent of coupling in this case is very high. Such a mechanism can be ruled out however, because if oxygen were responsible for the coupling reaction, then the

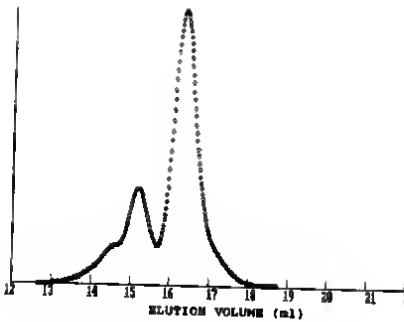


Figure 40. SEC trace of a P2VP sample which was prepared using a difunctional initiator, and then terminated by exposure to air

solutions stored at -78°C would be expected to contain some coupled product also.

It is well known that changes in the UV spectra of living polystyrene in THF occur when the solutions are allowed to age at room temperature (62). The main peak at 340 nm is seen to diminish in intensity, accompanied by the formation of a new peak at 535 nm. Sigwait and Tardi (59) have reported similar spectral changes in aged solutions of living P4VP in THF. No analysis of the molecular weight distributions in these systems was carried out, but an increase in viscosity upon aging was reported in the polystyrene system. This increase in viscosity was attributed to the physical association of the chain ends. The spectral changes observed in the polystyrene system are very similar to what is observed in the case of P2VP; however, in the polystyrene system, the disappearance of the original carbanion amounts to more than 60%, much more than is apparently observed in the P2VP system (~14%). This indicates that the side reactions occuring in both systems may be similar in nature, but that they occur to a much greater extent in the polystyrene system. Szwarc et al. (62) proposed a reaction scheme to account for the observed spectral changes in solutions of aged polystyrene. This scheme is depicted in Figure 41. The first step is the elimination of a metal hydride from the living chain end to produce a polymer with a terminal double bond. This intermediate is then deprotonated by other living chain

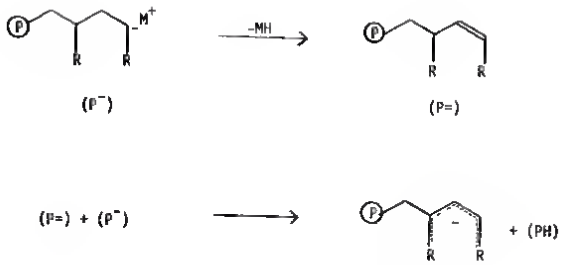


Figure 41: Reaction scheme proposed by Szwarc to explain side reactions in aged solutions of living polystyrene

ends, thus producing an allylic carbanion. Such a species is expected to be extremely stable, and is thought to be responsible for the new peak at 535 nm. This reaction scheme does not however, explain the doubling of molecular weight observed in aged solutions of living polymers.

It was thought that a similar sequence of reactions could be occuring in the P2VP system, and that the corresponding allylic anion in the P2VP system might be stable enough resist protonation by methanol. Upon subsequent exposure to air, this anion could then possibly undergo coupling by oxygen. In order to test this hypothesis, some of the solutions (Figure 37) were terminated with a mixture of methanol and HCl. The results are identical to those for the solutions terminated with methanol only, so this explanation is also ruled out.

It is very likely that the reaction scheme proposed by Szwarc and co-workers provides at least a partial answer to the problem. It seems plausible that a living polymer chain (P^-) could add to the double bond containing macromer intermediate (P=) formed after the lose of metal hydride, to give a living dimeric species (P^-P) (see Figure 42). Such an adduct would be expected to have a UV spectrum almost identical to that of the original living polymer, and thus could not be easily distinguished by UV. Such a reaction would most likely be reversible, owing to the high degree of steric interaction between the two chains. If the concentration of the intermediate containing the

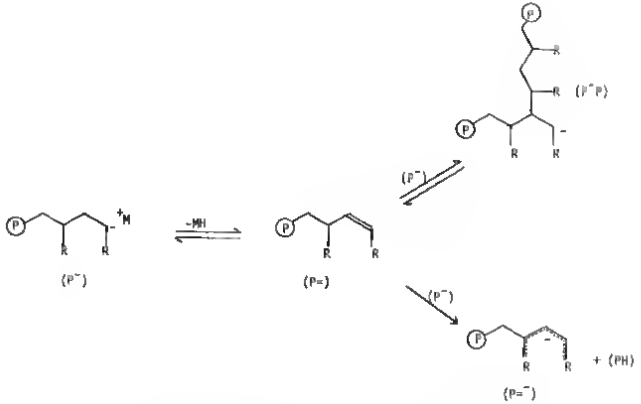


Figure 42. Proposed reaction scheme to explain the formation of a dimeric polymer in solutions of living P2VP stored at room temperature

terminal double bond (P=) were continually being depleted, due to the formation of the stable allylic carbanion ($P=^-$) then the concentration of the living dimeric adduct would be expected to decrease with time. This scheme is consistent with the observations on both the P2VP and polystyrene syetems, and supplements the scheme proposed by Szwarc. The above explanation would also explain the presence of the different end-group structures observed in the methyl region of the ^{13}C NMR spectrum of the polymers which had been stored at room temperature for two hours. Addition of $^{13}CH_3I$ to (P^-) gives the expected methylation products which show ^{13}C NMR peaks between 19 and 22 ppm. This is what is seen for the living P2VP solutions which were kept at -78°C. The products of methylation of the coupled polymer (P^-P), and the allylic carbanion ($P=^-$) would be expected to have structures significantly different from the "normal" end groups. In the case of ($P=^-$), the methylation may occur at either of two positions, both of which result in the formation of an allylic methyl group. These products would be expected to have chemical shifts different from those of the "normal" chain-end methyl groups, and thus may be responsible for the two new peaks (23.0 and 24.0 ppm) which are seen in the spectrum of the polymers which had been stored at room temperature for two hours.

The fact that the major portion of the original living ends do not disappear (as evidenced by UV) could possibly

be explained by a buildup of metal hydride in the solution, causing an equilibrium to be established, preventing further hydride elimination (see Figure 42). The observation that the extent of this reaction in the case of P2VP appears to be less than in the case of polystyrene seems reasonable, since the driving force for hydride elimination from the more reactive polystyryl anion is expected to be greater.

After the above explanation for the side reactions had been arrived at, it was realized that an almost identical explanation had been proposed several years earlier, in order to explain the presence of high molecular weight shoulders in the SEC chromatograms of linear polystyrene samples (23). Even though these reactions were noted, it appears that they were not studied in great detail. The extent of the dimerization reaction in that report appears to be similar to that found in the present work on P2VP, but it is difficult to be exactly sure since the SEC columns available at the time of that early work were inferior to those which are available today.

Comyn and Glaese (63) have reported the existence of side reactions in solutions of living poly(alphamethylstyrene). The proton abstraction reactions leading to the allylic anion are not possible in this system, because there is no methine proton. No mention of molecular weight distributions was made in this work. It is interesting that some of the side reactions in this system are reported to

be initiated by exposure to visible light. In order to test whether the side reactions which occur in the P2VP system are affected by light, an experiment similar to the ones described above was performed. In this experiment, the molecular weight distributions of living P2VP solutions which were aged for two hours at 25°C in the light and in the dark were compared. No noticeable differences were observed between the two solutions. This is consistent with the reaction scheme presented above.

The proposed scheme for the side reactions, however plausible, still requires further experiments in order to be proven conclusively. In particular, it would be of interest to use NMR to examine the structure of the chain ends more closely. Also of interest would be the study of the 2-isopropenylpyridine system, since the absence of a methine proton would presumeably prevent the disappearence of the living dimeric adduct through conversion to the allylic species. Addition of monomer to aged solutions of living P2VP would be of interest, since this would enable an evaluation of the relative amounts of species capable and/or incapable of further addition of monomer.

There are numerous cases in the literature where similar phenomena appear, but are either overlooked or attributed to some other cause. Takaki et al. (64) report "dimeric termination" in the reaction of living polystyryllithium and -potassium with benzyl chloride in THF. Gordon and Loftus (20) report obtaining a product with a bimodal

molecular weight distribution in the anionic polymerization of styrene carried out at room temperature in THF using various initiators containing both lithium and potassium as counterions. Eruesalimsky and Krasnoselskaya (60) report an increase in viscosity in solutions of living P2VP in toluene which were stored at -20°C. In Roovers and Toporowski's work on the synthesis of macrocyclic polystyrene (10), the SEC chromatogram of one of the linear precursors looks almost exactly like that of solutions of living P2VP which were aged for two hours at room temperature. It is very likely that the same side reactions are occuring in both the polystyrene and P2VP systems. Such reactions could cause problems and unexplainable results if their cause and importance are not realized. Fortunately, such reactions can be avoided if care is taken to always keep living polymer solutions at low temperatures (preferably -78°C or below).

REFERENCES

1. H. Jacobsen and W.H. Stockmayer, J. Chem. Phys. 18, 1600 (1950).

2. J.A. Semlyen, ed., "Cyclic Polymers", Elsevier, New York (1986).

3. G. Odian, "Principles of Polymerization", McGraw-Hill New York (1970).

4. M. Szwarc, "Carbanions, Living Polymers, and Electron Transfer Processes", Interscience, New York (1968).

5. M. Morton, "Anionic Polymerization, Principles and Practice", Academic Press, New York (1983).

6. F.M. Hoover, J. Macromol. Sci. Chem. Ed. A4(6), 1327 (1970).

7. J.A. Semlyen and K. Dodgson, Polymer 24, 391 (1983).

8. J.P. Kennedy, A.F. Fehervari and R. Faust, Polymer Preprints 28(1) (1987).

9. H. Hocker, Angew. Makromol. Chem. 100, 87 (1981).

10. J. Roovers and P.M. Toporowski, Macromolecules 16(6), 843 (1983).

11. H. Hocker and D. Gelser, Macromolecules 13(3), 653 (1980).

12. B. Vollmert and J. Huang, Makromol. Chem., Rapid Com. 1, 333 (1980).

13. F. Rempp, G. Hild and A. Kohler, E. Pol. J. 16, 525 (1980).

14. M. Morewetz, "Macromolecules in Solution", Wiley-Interscience, New York (1975).

15. J. Roovers, Polymer 20, 843 (1979).

16. W. Torekl, T.E. Hogen-Esch and M. Tekakl, Polymer Preprints 28(2), 343 (1987).

17. W. Toreki, T.E. Hogen-Esch and G.B. Butler, Polymer Preprints 29(2), (1988), accepted for publication.

18. B. Gordon, M. Blumenthal and J. Loftus, Polymer Bulletin 11, 349 (1984).

19. M. Fontanille, P. Guyot and P. Sigwalt, Ger. Offen DE 2726980, Dec. 29, 1977.

20. B. Gordon and J. Loftus, Polymer Preprints 27(1), 353 (1986).

21. W. Toreki, T.E. Hogen-Esch and G.B. Butler, Polymer Preprints 27(1), 355 (1986).

22. R.P. Quirk, Polymer Preprints 27(1), 188 (1986).

23. W.A.J. Bryce, I.G. Meldrum and G. McGibbon, Polymer 11, 394 (1970).

24. J. Klein, A. Medlik and A.Y. Meyer, Tetrahedron 32, 51 (1976).

25. M.J. Mencer and Z. Grubisic-Gallot, J. Liq. Chrom. 2(5), 649 (1979).

26. W.W. Yau, H.J. Stoklosa and D.D. Bly, J. Appl. Pol. Sci. 21, 1311 (1977).

27. T.E. Hogen-Esch in "Advances in Physical Organic Chemistry" vol. 15, V. Gold and D. Bethell, eds. Academic Press, New York (1977).

28. P. Rempp, P. Lutz and C. Strazielle, Polymer Preprints 27(1), 190 (1986).

29. P. Rempp, G. Hild and C. Strazielle, Eur. Pol. J. 19(8), 721 (1983).

30. B.B. Zimm and W.H. Stockmayer, J. Chem. Phys. 17, 1301 (1949).

31. E. Casassa, J. Pol. Sci. A3, 605 (1965).

32. G. ten Brinke and G. Hadziioannou, Macromolecules 20, 489 (1987).

33. G.B. McKenna et al., Macromolecules 20, 498 (1987).

34. R.C. Jordan and M.L. McConnell, in "Size Exclusion Chromatography (GPC)" ACS Symposium Series #138, T. Provder ed., ACS, Washington, DC (1980).

35. J. Roovers, J. Pol. Sci.-Pol. Phys. Ed. 23, 1117 (1985).

36. V. Bloomfield and B.H. Zimm, J. Chem. Phys. 44, 315 (1966).

37. M. Fukatsu and M. Kurata, J. Chem. Phys. 44, 4539 (1966).

38. J. Shimada and H. Yamakawa, J. Pol. Sci.-Pol. Phys. Ed., 16 (1978).

39. J. Roovers, Polymer 20, 843 (1979).

40. J.H. Gibbs and E.A. DiMarzio, J. Chem. Phys. 28, 373 (1958).

41. J.A. Semlyen, S.J. Clarson and K. Dodgson, Polymer 26, 925 (1987).

42. E. DiMarzio and C. Guttman, Macromolecules 20, 1403 (1987).

43. J. Roovers, Macromolecules 18, 1359 (1985).

44. R. Fouss and W.N. Maclay, J. Pol. Sci. 6(5), 511 (1951).

45. J. Morcellet-Sauvage and C. Louchaux, Die Mak. Chemie 176, 315 (1975).

46. P.J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithica New York (1953).

47. D.J. Worsfold and S. Bywater, in "Recent Advances in Anionic Polymerization", T.E. Hogen-Esch, ed., Elsevier, New York (1987).

48. J. Roovers and S. Bywater, Macromolecules 5(4), 384 (1972).

49. N. Hadjichristidis and L.J. Fetters, Macromolecules 13, 191 (1980).

50. B. Zimm and W.H. Stockmayer, J. Chem. Phys. 17, 301 (1949).

51. J. Mazur and F. McCrackin, Macromolecules 10(2), 326 (1977).

52. B.H. Zimm and R.W. Kilb, J. Pol. Sci. 37, 19 (1959).

53. M. Morton et al., J. Pol. Sci. 57, 471 (1962).

54. S. Banks and J. Sturges, J. Organometallic Chem. 156, 5 (1978).

55. R. Morrison and R. Boyd, "Organic Chemistry", 4th ed., Allyn and Bacon, Boston (1978)

56. C. Meverden and T.E. Hogen-Esch, unpublished results

57. C. Meverden and T.E. Hogen-Esch, Mak. Chem.-Rapid Com. 4, 563 (1983)

58. A.H. Soum and T.E. Hogen-Esch, Macromolecules 18, 690 (1985)

59. P. Sigwalt and M. Tardi, Eur. Pol. J. 9, 137 (1971)

60. B. Erussalimsky and I. Krasnoselskaya, Mak. Chem.-Rapid Com. 6, 191 (1985).

62. M. Szwarc, G. Spach and M. Levy, J. Chem. Soc. C, 355 (1962).

63. J. Comyn and M.D. Glasse, J. Pol. Sci.-Chem. Ed. 21, 207 (1983).

64. M. Takaki, R. Asami and Y. Kuwata, Polymer Journal 11(5), 425 (1979)

BIOGRAPHICAL SKETCH

William Torski III was born on April 19, 1961, in Philadelphia.

He graduated from Pennsbury High School in Fairless Hills, Pennsylvania in June of 1979.

He began attending the University of Delaware in August of 1978 and graduated with a Bachelor of Science degree in chemistry in June of 1982.

Since August of 1982, he has been pursuing graduate studies in polymer chemistry at the University of Florida.

I certify that I have read this study and in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Theo E. Hogen-Esch, Chairman
Professor of Chemistry

I certify that I have read this study and in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Christopher D. Batich
Associate Professor of
Materials Science and Engineering

I certify that I have read this study and in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

George B. Butler
Professor Emeritus of
Chemistry

I certify that I have read this study and in my opinion it conforms to acceptable standards of scholariy presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

John G. Dorsey
Associate Professor of
Chemistry

I certify that I have read this study and in my opinion it conforms to acceptable standards of schoiarly presentation and is fuliy adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

James D. Winefordner
Graduate Research Professor of
Chemistry

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fuifiiment of the requirements for the degree of Doctor of Phiiosophy.

Dean, Graduate School

April 1988